METALLURGIA

The British Journal of Metals

(INCORPORATING THE METALLURGICAL ENGINEER)

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The articles in this Journal are indexed in *The Industrial Arts Index*

Subscription Rates throughout the World - - 24/- per annum, Post free

Published monthly by THE KENNEDY PRESS, LIMITED.

Registered Office: 31, King St. West, Manchester, 3. *Telephone:* BLA 2084. *Telegrams:* "Kenpred," Manchester.
LONDON OFFICE: 21, Bedford Street, W.C.2. *Telephone:* Temple Bar 2629.

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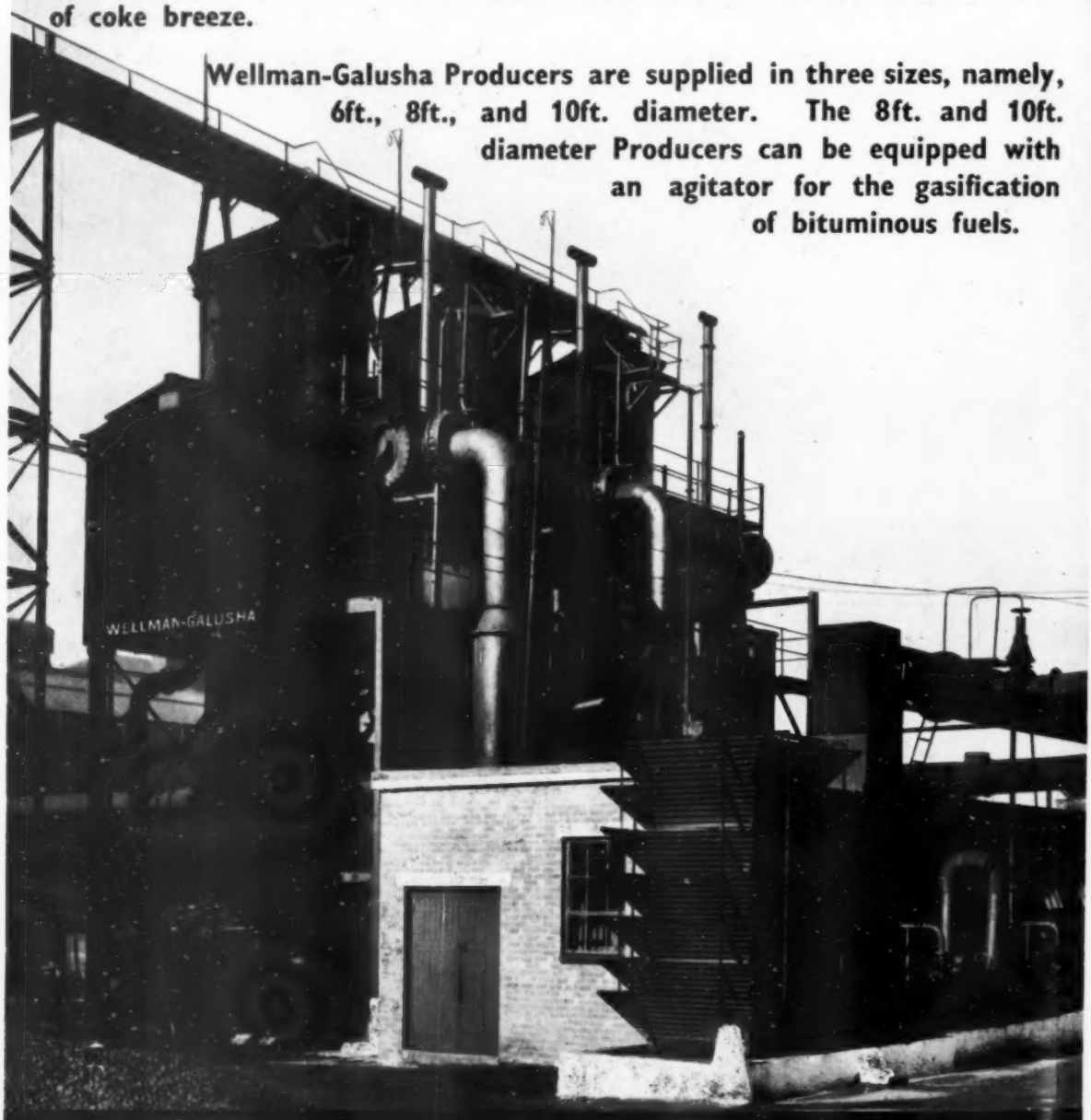

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METALLURGIA

THE BRITISH JOURNAL OF METALS

INCORPORATING THE "METALLURGICAL ENGINEER."

DECEMBER, 1950 Vol. XLII No. 254

The Raw Materials Problem

THE year that is almost completed has been a difficult one for producers and consumers of both ferrous and non-ferrous metals. At the beginning of the year the iron and steel industry had made such remarkable progress that the home demand was being fully met and it was anticipated that control of this vital material would soon cease. Indeed, for a time, it seemed that a continuing increase in production would result in a surplus before the year was out. However, a distinct change for the worse in the international situation has brought about an increased demand and all the productive capacity of the industry is being rapidly consumed or allocated to defence programmes.

We take this opportunity of extending Cordial Greetings to all Readers and Sincere Good Wishes for Christmas and the coming New Year.

In addition to the rapidly deteriorating international situation the political position at home has been far from happy and the uncertainty that has prevailed, and still exists, in the iron and steel industry, is neither good for the nation nor for the industry. Fortunately the industry has concentrated its attention on the production of iron and steel and has invested the major part of its profits in the installation of new, or in modernising existing, plant and equipment, despite the existing unfavourable political influences, with the result that production has been maintained at the highest level. Again, production targets have been exceeded, which demonstrates the soundness of managerial planning and the co-operation that exists at all levels in the industry.

Although the iron and steel industry will have many problems to meet in the coming year and the political situation may seriously interfere with future developments, the position of the non-ferrous metals industry is alarming. In this case practically all the raw materials are imported and, due to the short-sighted policy of the Government, the consuming industries have been living from hand to mouth and, in consequence, they are quite unprepared to meet the demands arising from the deteriorating international situation. Unless the Government acts with speed and decision, some sections of industry may soon be unable to carry on. Whether the present position is due to the failure of the Government to look sufficiently far ahead to meet industry's needs or to its desire to effect a balanced economy by curtailing imports there seems little doubt that it has to some extent been caught unprepared by the present problems.

A statement on the grave supply position of certain non-ferrous metals was made by the Minister of Supply early this month. It was made in the form of a written reply to a Parliamentary Question and there has been no opportunity for supplementary questions or for Parliamentary discussion; it is not surprising, therefore, that the British Non-Ferrous Metals' Federation, on behalf of its members, places the supply position in its right perspective. Reference is made to the prospective shortages of copper and zinc on which information was disclosed, and it is stated that, if the position is not rapidly alleviated by national or international action, the result during the next few months will be widespread redundancy of labour and a serious decline in production in all metal making and metal using industries. The impact of this is all the graver in view of the assurance given by the Ministry of Supply on August 25th last that . . "ample stocks of copper, lead, and zinc will be available to meet consumers' current requirements as they arise . . ."

The Federation agrees with the Minister that measures to ensure proper distribution are under consideration in consultation with the industry on the crisis measures which have now to be taken and recognise the co-operative spirit of the Minister and his advisers in this matter, but it emphasises that this consultation extends only to what has now to be done. The Minister of Supply has not at any time called for the advice of metal consumers in carrying out his bulk supply policy. Although a post-mortem on the present position would be futile the Federation is justified in expressing the view, widely held in industrial circles, that if the Minister had, in the past, followed a bolder and more imaginative purchasing policy, as private industry would have done, industry would not now be in such a grave position.

In a recent statement by the President of the United States and the Prime Minister, industry is promised that international action will be taken to ensure the equitable distribution of basic raw materials. This looks alright on paper, but at the time of writing there is no indication how it will be given effect. Already steps have been taken to dole out, on a percentage basis, supplies of raw materials available, but uncertainty prevails.

The scarcity of metals essential to rearmament is particularly acute and it seems that this is mainly due to America's entry into the world metal market on a vast scale, but this is not by any means the whole story; world metal markets have been booming for some considerable time and delayed action on the part of this country is largely responsible for the present impasse. It is true, of course, that the policy adopted by the Government has been concerned primarily with national economy: without adequate supplies of raw materials, however, industry is in a hopeless position to manufacture on a scale which will maintain the level of exports desired and, with a defence programme to be given effect in addition, the economy of the country must suffer a serious setback.

It is hoped that steps will be taken to halt the rapidly deteriorating international situation and to restore conditions in which peaceful pursuits can prevail.

The Institute of Metals

Appeal for Financial Support

YEARS ago the work of the Institute of Metals could be maintained on the revenue from the subscriptions of its members and the sales of its publications, but the rapid advances in the science of metallurgy and the technological developments in the industry in recent years, coming at a time when the costs of all services are continually increasing, have made demands on the Institute for the publication of papers, etc., the costs of which members are now unable to sustain. There are also new services to science and industry which this Institute is being pressed to perform which it cannot at present undertake because of its financial position. Some indication of the rising costs since the war are shown by this Institute's regular expenditure in 1949–50 which was £25,660 compared with £8,179 in 1939–40.

The Council has taken energetic steps to bridge the gap between income and expenditure, not only by increasing the rate of subscription but also by expanding sources of revenue and exercising all reasonable economy consistent with the energetic prosecution of the Institute's work. Despite all that has been done the deficit on regular income is now about £2,000 a year, and various items of cost must be expected to increase still further. Apart from a further substantial increase in the rate of subscription, which would unduly burden members, there seems no prospect of meeting expenses except by a drastic curtailment of the Institute's activities, which would seriously react on the healthy progress of non-ferrous metallurgy and of the industries concerned at a time when it is of vital importance that they should be vigorously developed.

It is confidently believed that industry will not wish this Institute, which has become a vital factor in the progress of the science and practice of non-ferrous metallurgy, to reduce the scale and effectiveness of its work or to draw continually on its accumulated funds and so create a situation—already becoming serious—which would lead to a financial crisis. It is also believed that industry would not wish this important service to depend to such a large an extent on the voluntary contributions of persons who are mainly employees in industry. With these thoughts in mind the Council of this Institute is making an appeal to the non-ferrous metals industries, in the widest sense, for regular financial support under covenants of not less than seven years, so that the Institute could recover income tax on the contributions so received. An additional income of not less than £5,000 per annum is required to place the Institute in a reasonably safe position, to enable it to carry out its regular work and also to undertake, without embarrassment, such further activities as will promote its aims.

This appeal, which is addressed to a wide field of producer, fabricator and user firms, gives the industry the opportunity to acknowledge the benfits which have accrued as a result of the Institute's activities, particularly in the scientific welfare and advancement of all the industries concerned with the manufacture, treatment and use of non-ferrous metals and alloys. We have no hesitation in recommending this as a very worthy cause and to advise firms or individuals interested to communicate with Lt.-Col. S. C. Guillan, Secretary, Institute of Metals, 4, Grosvenor Gardens, London, S.W.1, who will supply a form of covenant.

The Nickel Industry in 1950

DESPITE the fact that nickel was in tight supply during the last six months, the amount available for distribution and Governmental stockpiling in 1950 was the largest for any peace-time year in the history of the Canadian nickel industry. It is expected that nickel output by the Canadian producers, International Nickel and Falconbridge Nickel Mines, Ltd., for the year 1950, will approximate 250,000,000 pounds. In the latter part of June, prior to the Korean conflict, when it became apparent that the demand for nickel would exceed the available supply, a voluntary rationing programme was put into effect. Although nickel, like other metals, remains in tight supply, military requirements are being met in full and shipments are being made to Government stockpiles. The trade's civilian requirements continue, however, to take the major portion of the world's supply.

In the United States early this month, an order was issued by the National Production Authority limiting the non-military consumption of nickel in the first quarter of 1951 to 65% of the average quarterly rate of consumption during the base period comprising the first six months of 1950. The order is stated to be designed to maintain equitable distribution, through normal channels, of that amount of primary nickel remaining after meeting the requirements of the national defence.

International Nickel's production of nickel for the past six months has been maintained at maximum capacity. This has only been possible through a development and expansion programme to provide greatly increased underground ore facilities to replace open pit ore, depleted during World War II. The broad mining development and expansion programme has entailed expenditures in recent years of some $90,000,000, of which over $40,000,000 have been spent since the end of World War II. This programme will require further large capital expenditures during the next several years to permit maintenance of current capacity production of nickel as the end of supplies from the Frood-Stobie open pits approaches.

Canada, the world's predominant producer of nickel since the early part of this century, continued to furnish the industrial world with the major portion of its requirements. This year's nickel output of the French New Caledonian deposits is reported to have been sufficient to meet the requirements of French industry. No information is available on Russia's 1950 production of nickel. In September it was reported that the United States Government was planning to reactivate its idle nickel facilities at Nicaro, Cuba, which were closed early in 1947. The production of this plant for the preceding year, was reported at approximately 25,000,000 pounds.

In the second quarter of the year major increases in costs for refined nickel required International Nickel to raise its United States base price of electrolytic nickel to 48c per pound, including the United States import duty. Prices in other markets were adjusted correspondingly. The increase brought the price of nickel to a level about 40% above the average price prevailing for all markets in the pre-war years.

THE Bessemer Medal for 1951 of The Iron and Steel Institute has been awarded to Mr. Ben Fairless, President of the United States Steel Corporation, in recognition of his distinguished services to the iron and steel industry.

The Iron and Steel Institute

Autumn General Meeting in London

THE Autumn Meeting of The Iron and Steel Institute was held on Wednesday and Thursday, November 15th and 16th, 1950, at the Offices of the Institute, 4, Grosvenor Gardens, London, S.W.1. In the absence owing to indisposition of the President, Mr. J. R. Menzies-Wilson, the chair was taken on the Wednesday and Thursday mornings by Dr. C. H. Desch, F.R.S., Past President, and on the Wednesday afternoon by Mr. James Mitchell, C.B.E., the Honorary Treasurer.

The Chairman referred to the deaths of Col. Sir Charles Wright, Past President, and Sir Edward George, an Honorary Vice-President, both of whom had done much for the Institute. The meeting stood in silence for a short time as a token of respect.

After welcoming members and visitors, Dr. Desch announced that the Council had awarded the Sir Robert Hadfield Medal for 1951 to Mr. W. Barr, of Colvilles, Ltd.

In the President's absence, the Secretary, Mr. K. Headlam-Morley read the remarks he would have made had he been present. To the small and distinguished list of Honorary Members, the Council had nominated Dr. C. H. Desch, F.R.S. Dr. Desch had been a member of the Institute for 37 years, and had served on the Council for 26 of them. He was a Past President and Bessemer Medallist, and was held in high esteem and warm affection.

Members would, no doubt, be pleased to hear that Dr. Johan Görrissen, of Norway, had received at the hands of our Ambassador in Norway, the King's Medal for Courage in the Cause of Freedom, and that Dr. Magnus Tigerschiöld had been awarded the Carl Lueg Medal of the Verein deutscher Eisenhuttenleute.

The Council had accepted an invitation from the Eisenhütte Oesterreich to hold a Special Meeting in Austria next September. This would precede a Meeting of the Institute of Metals to be held in Italy.

The Annual General Meeting for 1951 had been arranged to coincide with the Festival of Britain and would be held May 30th and 31st, when it was hoped to arrange an interesting programme.

Mr. Menzies-Wilson's last task was the pleasant one of announcing that the Council had nominated Mr. Richard Mather to succeed him as President.

Technical Papers

Following the business meeting a number of papers were presented and discussed; a brief account of these is appended below.

THE THERMODYNAMIC BACKGROUND OF IRON AND STEELMAKING PROCESSES. II.—DEOXIDATION*

By Dr. F. D. Richardson

The interactions which occur between liquid iron, dissolved oxygen, and a dissolved alloying element make deoxidation a complex process even in the simplest system. In practice other solutes, such as carbon and silicon, are always present in the system. In addition, the deoxidation products frequently interact with each other, and with the refractories, to form complex slags. In this paper, the thermodynamic principles involved in deoxidation are discussed, and a critical survey is made of the thermodynamic data available for solutions of oxygen and alloying elements in liquid iron. The main deoxidation equilibria are summarised in two diagrams for 1,600° and 1,540° C. The results discussed are based on controlled studies of relatively simple systems, so that they cannot be applied rigidly to works conditions. On the other hand, any understanding or explanation of the results obtained in practice should not run counter to the physico-chemical basis outlined.

As would be expected, the interaction of an alloying element with dissolved oxygen increases markedly with the heat of formation of its oxide, although carbon appears to behave in an anomalous manner, for which it is difficult to find an explanation. Since carbon is frequently present in systems which are treated with deoxidisers, it is interesting to note that elements which have carbide forming tendencies, but which interact weakly with iron, appear to have their activity coefficients lowered by carbon, whilst those which interact more strongly with iron than with carbon have them raised. The choice of a deoxidiser obviously depends on how low an oxygen concentration it is desired to reach, and on the secondary effects of the deoxidising elements on the properties of the solid metal. The more negative the value of $\triangle G_{1600°C.}$ (free energy of formation at 1,600° C.) for the oxide, the greater are the deoxidising powers of the element concerned, whilst the greater the value of $\triangle H_{25°C.}$ (heat of formation at 25° C.) for the oxide, the more markedly does the fall in temperature from 1,600°–1,540° C. assist deoxidation. Besides the influence of falling temperature of the liquid iron, a further marked increase in deoxidation is to be expected on solidification due to the segregation of both oxygen and the deoxidising elements from the freezing solid into the neighbouring liquid.

STUDIES IN THE DEOXIDATION OF IRON DEOXIDATION BY ALUMINIUM*

By H. A. Sloman, M.A., F.R.I.C., F.I.M., and E. L. Evans, B.Sc.

In this paper the results are presented of the microscopical and analytical investigation of 19 ingots made by adding quantities of iron oxide and aluminium to melts of pure iron, *in vacuo*. The inclusions formed on deoxidation of iron by aluminium consist mainly of α–alumina when the added aluminium is stoichiometrically in excess of the dissolved oxygen. When it is not in excess, the inclusions also contain hercynite ($FeO.Al_2O_3$), and sometimes magnetite, (Fe_3O_4). When oxygen is in large excess, hercynite occurs mainly as dark idiomorphic particles within spherical wüstite inclusions. The mechanism of formation can be explained by the existing knowledge of the phase

* *J.I.S.I.* October, 1950.

* *J.I.S.I.* May, 1950

relationship in the Fe–O–Al system. In an appendix by O. Kubaschewski, known data are used to derive a value for the equilibrium constant of the deoxidation equation $2\ Al + 3\ FeO = 3\ Fe + Al_2O_3$.

Joint Discussion

A number of interesting points were raised in the discussion which was opened by Sir Charles Goodeve. Sir Charles pointed out that the lowering of the activity of one element by another was mutual, a point which was fundamental to the conception of preferential positioning of atoms on adding a deoxidiser. On the question of the type of inclusions formed, he felt that considerably better separation of alumina would be obtained if it could be made to form into proper crystals instead of gel-like clusters. Both he and Mr. O. Kubaschewski, who followed, emphasized that the apparent increase in complexity of the subject of deoxidation would eventually lead to practical results. Mr. Kubaschewski said that a mass-action constant of a slag-metal system could be calculated from the activities of the elements dissolved in the metal, at concentrations of about 1% by weight, and the free energy of formation of the slag, provided that (i) the fundamental data were accurately known; (ii) the mutual interaction of the dissolved substances were known quantitatively; and (iii) Henry's law were strictly valid for the dissolved elements between 0 and 1%. After discussing some of the calculations in the light of further information and considerations, he concluded that most of the queried results obtained by Dr. Richardson could be explained.

Dr. R. V. Riley said that although there might be grounds for querying the melting of iron in an alumina crucible, in view of the possibility of aluminium being reduced from the crucible and dissolved in the steel, his experience with cast iron suggested that this was not necessarily so, due to the fact that inclusions had a habit of being moved to the sides of the crucible.

Dr. A. J. E. Welch commented on the constitution of solutions of oxygen and alloying elements in liquid iron. Dr. Richardson had suggested that the behaviour of nickel was almost ideal, due to the similarity between nickel and iron, but that titanium would not be expected to behave ideally due to the formation of intermetallic compounds. Was the assumption that, because intermetallic compounds separated on solidification, the activity coefficient in liquid solution was somewhat reduced justified?

Mr. W. A. Smith submitted data collected on the steel plant which he hoped would help to solve the problems associated with determining the equilibrium conditions of aluminium with oxygen in molten iron. They had been keenly disappointed that valuable fundamental work had not, in their case, producing low-carbon killed coarse-grained steels, so far proved of any practical value. The methods of addition of deoxidisers in use allowed 90% to be used up on the slag or ore rather than the steel. It would be interesting to learn the experience of those making rimmed or balanced ingots, or controlled grain size killed steel.

Dr. P. Herasymenko, after pointing out that results obtained from laboratory melts agreed with the distribution of chromium and manganese between metal and slag in the acid open-hearth furnace, probably as a result of the highly oxidising atmosphere being neutralised by the carbon monoxide from the boil just above the slag, proceeded to calculate the deoxidation equilibria for vanadium and aluminium from their distribution between metal and slag.

Mr. R. E. Lismer thought that the ingots used by Sloman and Evans should have been cooled slowly in order to produce larger inclusions of the reaction type. The segregation of alumina particles into massive clusters might have been due to uneven initial dispersion of the aluminium addition. A similar effect had been noted in certain other ingots prepared by adding excess aluminium to highly oxidised metal.

In reply Dr. Richardson agreed with Sir Charles Goodeve on the question of mutual lowering of activities. To Dr. Welch's query on intermetallic compounds, he could only say that they did provide a guide to what might happen when alloying elements were added to liquid iron.

Mr. E. L. Evans, in replying on behalf of Mr. Sloman and himself, pointed out that the N.P.L. Mark II iron was originally prepared in sintered alumina crucibles and contained no aluminium in addition to that associated with the oxygen.

THERMODYNAMIC ASPECTS OF THE MOVEMENT OF SULPHUR BETWEEN GAS AND SLAG IN THE BASIC OPEN-HEARTH PROCESS*

By F. D. Richardson and G. Withers

The total quantity of sulphur passing through the open-hearth furnace in the furnace gases is frequently ten or more times the total quantity charged in the ingoing liquids and solids. The importance of minimising, as far as possible, the pick-up of sulphur by the melting metal is well recognised, and it is generally agreed that this objective can be achieved by keeping gas conditions within the furnace as oxidising as possible, so that a protecting oxide layer is formed as rapidly as possible. Once the charge is melted and covered with a basic slag, conditions are quite different. If the slag picks up sulphur, it will obviously be hindered in its work of desulphurising the metal, a matter of considerable moment in the production of low-sulphur steels with high-sulphur gases. In this paper, an attempt is made to calculate the conditions under which this pick-up by the slag can be avoided. A theoretical study is made of the sulphur equilibrium between a basic slag containing sulphur in the furnace gases in the open-hearth process. It is concluded that the higher the slag temperature and the more complete the degree of combustion of the gases coming into contact with the slag surface, the less chance there is of the slag picking up sulphur from the gas phase. The combustion limits which are required at the slag surface in the presence of gases of various sulphur contents, to avoid pick-up in the refining period, are calculated, and it is suggested that if these limits can be exceeded in practice, it should be possible to pass sulphur from metal to gas via the slag at the same time as oxygen is passed from gas to metal.

Discussion

Dr. U. R. Evans, in opening the discussion, emphasised the importance of producing low-sulphur steel, since sulphur produced corrosion in some, though not all, circumstances. The practical aspects were dealt with by Dr. Matuschka who confirmed the influence of excess air in the open-hearth atmosphere, and of temperature. In Austria, where all-basic furnaces were widely used, conditions for gaseous desulphurisation were more favourable. Dr. P. T. Carter referred to the influence of the gas evolved during the lime and ore boils on the composition of the furnace atmosphere and, hence, on the slag-gas equilibria. Dr. A. H. Leckie pointed out that the present method of adding a large amount of lime meant that sulphur would be picked up from the gas in parts of the bath where the atmosphere was reducing. The paper suggested that one could get sulphur removal by using a thin slag layer and burning the sulphur off the surface; he would like to see the idea put to the test in the open-hearth furnace.

* *J.I.S.I.* May, 1950.

Dr. Richardson in reply, commented on Dr. Leckie's thin slag layer suggestion, and pointed out the importance of having the gas situation right, otherwise the thin slag layer would operate adversely.

THE EFFECT OF COLD WORK ON STEEL*

By J. H. Andrew, H. Lee, P. L. Chang, B. Fang and R. Guenot

The work-hardening behaviour of carbon steels is known to be different from that of pure iron in many respects, and since the obvious difference between them lies in the presence of carbon, it was thought that the unusual features associated with the work-hardening properties of steel may be considered from a metallurgical point of view. With this in mind the authors, in an earlier paper, drew attention to certain features and compared them with the effect of quenching, the hypothesis being advanced that austenite was formed in steel during cold-working. For normal forms of cold-working, the austenite theory was not generally accepted as proved, although there are indications that with dynamic loading where the deformation is extremely rapid and localised, or in the case of working which involves intense heat due to surface friction, the formation of martensite does occur. At the same time, the various effects of internal strains upon physical and mechanical properties of steel are not sufficiently realised. It was with this in mind that the work reported in the present paper was undertaken, experiments being carried out on a much more extensive scale and covering both normal and rapid rates of cold working.

The experimental work was carried out by several groups of workers at the University of Sheffield and the results are sectionalised according to the groups. A range of steels of varying carbon content, together with a few low-alloy steels, was utilised for this purpose. Most of the cold-working was in the form of wire drawing.

Unlike low-carbon iron, high-carbon steels show a rapid increase in hardness towards the higher reductions, whilst the initial shape of the work-hardening curve depends on the initial treatment. The cold-worked high-carbon steels, again unlike iron, show a marked hardening on tempering up to 300° C.

The most marked change observed in dilatation experiments in the longitudinal direction on cold-drawn steel wires is an expansion between 150° and 450° C. The change is mainly directional and is more pronounced with the higher carbon contents, and with pearlitic rather than sorbitic initial structures.

On cold-working steel the maximum decrease in density is about 0·2–0·3% and recovery on tempering takes place between 400°–700° C. With ingot iron, the density decrease and recovery appear to vary with the amount of inclusions present.

With a 0·7% C. steel, cold-drawn beyond 50% reduction, the cementite Curie point is markedly affected, and at reductions over 90% the thermo-magnetic curve shows no discontinuity corresponding to the normal cementite Curie point. Such an effect has also been observed with tempered martensite. At room temperature, the magnetic saturation is apparently unaffected by cold-working. X-ray examination of a cold-drawn high-carbon steel shows that the intensity of cementite lines is appreciably weakened when reductions exceed 50%, and micrographic observations confirm that cold-worked steels are prone to graphitisation on sub-critical annealing.

The electrical resistivity, measured in the longitudinal direction, increases when iron or low-carbon steels are cold-drawn and decreases in the case of high-carbon steels, the decrease being greater the higher the carbon content. On tempering cold-drawn wires, the resistivity of low-carbon iron increases continuously up to tempering temperatures of 550°–600° C., whilst with high-carbon steel a small increase occurs over the range 150°–450° C. with a maximum at 250°–300° C. Experiments on the effect of cementite distribution show that the lowering of longitudinal resistivity is less with a sorbitic than a pearlitic structure.

After cold-working, both the macro-strains (as defined by a change in X-ray ring diameter) and the micro-strains (as defined by line-broadening) are greater in the case of high-carbon steel. In the low-carbon iron, the macro-strains measured in the transverse direction vary from compressive near the surface to tensile at the centre, such strains being mainly due to the presence of body stresses. With a cold-drawn high-carbon steel, the presence of textural stresses gives rise to macro-strains such that ferrite is apparently under uniform compression in the longitudinal direction with the cementite under tension, with reversal of sign in the transverse direction. The recovery of macro-strains is consistent with the dilatation results.

The results of a series of experiments in which the specimen was deformed by a falling weight, confirm that the deformation is extremely localised and that the white band formed contains austenite and martensite.

X-ray examination of high-carbon and alloy steels after cold-working by compression has failed to show the presence of austenite on unfractured test-pieces, but had shown that it may be formed on the surface of shear fractures. An X-ray investigation of the influence of severe cold-working on cementite in steel has produced evidence of large residual strains in the cementite and a tendency towards preferred orientation.

An electrolytic method of investigation has shown that the rate of hydrogen diffusion is decreased by cold-work whilst the saturation is increased. In heat-treated specimens, there are indications that the state of division and distribution of the cementite plays a part in determining the rate of hydrogen diffusion.

In considering the results of the various investigations, it is concluded that the earlier austenite theory is only tenable in special cases where intense local heat is generated during deformation. In normal cold-working processes, the change of properties is explained in terms of the effects of various internal strains in ferrite and cementite. The effect of such strains, and of those arising from the mutual restraint between ferrite and cementite, has not been sufficiently realised. The increased hydrogen saturation in cold-worked steels has been correlated with X-ray line broadening, thus supporting the view expressed in an earlier paper that the hydrogen introduced into steel at room temperature is mainly accommodated in occluded form at the crystallite boundaries or mosaic disjunctions.

Discussion

Mr. H. H. Burton, who opened the discussion, referred to the section on hydrogen diffusion, and suggested that further work was needed to determine whether the effects of cold-work on diffusion were directional, as he thought. In

* *J.I.S.I.* June and August, 1950.

discussing the observed decrease in hydrogen diffusion rate, the authors had attributed it, in part, to the occlusion of hydrogen in molecular layers at mosaic boundaries or disjunctions: had they explored the possibility of its being associated with inclusions, in view of the evidence that even hot-rolling could leave little voids at the tail-end of silicate inclusions in particular. Finally, Mr. Burton suggested that structural differences might effect diffusion.

The section dealing with dimensional changes had interested Dr. R. H. Greaves, who pointed out the importance of results in such applications as springs and tie-rods made from cold-worked material, particularly when used at elevated temperatures. Interesting examples of this sort of effect had arisen in connection with wire-wound gun tubes, where the wire had to withstand the heating it received on firing, without losing tension. A number of steels were tested, and in each case, heating to a suitable temperature before winding, by effecting the dimensional change, greatly reduced the loss of tension on firing.

Mr. F. R. N. Nabarro did not think that a point of inflection in the hardness—reduction-of-area curve was itself significant, but a study of other properties did seem to suggest a change in the mechanism of deformation at about 40% reduction. Referring to the suggestion that the cementite must undergo an amount of plastic yielding sufficient to allow the ferrite to recover elastically, he commented that there was no need to draw such an unwelcome conclusion from the observations. Dr. Nabarro regarded the strain as being produced by shearing stresses across the interfaces between ferrite and cementite

On the question of hydrogen diffusion, Mr. A. G. Hock said that in passing hydrogen electrolytically, the resistance which had to be overcome at the surface might overshadow the resistance to diffusion through the steel.

References to the effect of other elements on the cold-working behaviour were made by Dr. B. Matuscha, who asked about the influence of traces of alloying elements arising from scrap, whilst the Chairman (Mr. James Mitchell) asked why no reference had been made to nitrogen which so greatly influenced cold-working behaviour.

In reply, Dr. H. Lee agreed with Mr. Burton that the hydrogen-diffusion effect of cold-work was directional, and added that there was a possibility of the diffusion rate varying with crystallographic direction in iron. Referring to Mr. Burton's questioning of a statement that chromium decreased the diffusion rate, Dr. Lee agreed that it was open to criticism on the evidence presented in the paper, but subsequent experiments had confirmed it. Dr. Lee thanked Mr. Nabarro for his suggestion that cementite need not deform to allow the ferrite to recover elastically, but one had to judge, not from one result, but, from all the results in the paper and he thought Mr. Nabarro would agree that there was good evidence in the paper to show that strain did exist in cementite. Dr. Lee agreed with Mr. Hock that surface reaction was important in diffusion work and in experiments carried out at various temperatures, the importance of surface reaction was found to be greater at the lower temperatures.

ATLAS OF ISOTHERMAL TRANSFORMATION DIAGRAMS—SPECIAL REPORT No. 40

Prepared by a Group of the Thermal Treatment Sub-Committee of the Metallurgy (General) Division of the British Iron and Steel Research Association, this report comprises isothermal transformation diagrams of 24 steels in the British Standards Institution En Series. Each diagram is accompanied by details of the tests, supplementary isothermal data, and comments relating to steels within the En specification range.

Discussion

Some indication of the interest in this report can be gained from the fact that 11 speakers took part before the discussion had to be closed. In opening, Dr. N. P. Allen said he was glad the authors had avoided giving elaborate calculations for predicting the behaviour of steels under specified conditions of cooling: unless made with the utmost circumspection, such calculations could be very misleading. The effect of variation from cast to cast and of position in bar or billet cross-section were discussed by Dr. W. Steven, from which it was apparent that a generous safety factor should be applied in deriving a heat-treatment time from isothermal transformation diagrams. In recommendations for future work, Dr. Steven included a more detailed study of the martensite reaction and a set of continuous cooling diagrams on the same series of steels. Mr. C. L. M. Cottrell drew attention to the use of the diagrams for determining the welding procedure necessary to prevent martensite formation in the heat-affected zone, whilst Mr. H. Allsop suggested that an important practical application of isothermal-transformation diagrams concerned the controlled cooling of forgings, etc., from hot-working temperatures, and emphasized the importance of the finishing temperature on subsequent behaviour. The diagrams could form a basis for fixing heat-treatment schedules, in the opinion of Mr. C. C. Hodgson who also felt that curves for case-hardening steels would be useful in view of the probable increase in the use of isothermal annealing and martempering in that field. After showing a few slides illustrating the sort of apparatus used, Mr. E. Johnson said that whilst certain factors had to be taken into account, there was no cause for excessive caution in using the curves practically. In view of the wide range of industrial steels, to publish the S-curves of all would, as Mr. C. E. Mavrocordatos said, be a gigantic task. He suggested that the En series should be completed, after which effort should be concentrated on a few basic compositions to which judicious additions of alloying elements could be made to evaluate their effect. Both Mr. Mavrocordatos and Mr. P. T. Moore referred to the preliminary separation of pro-eutectoid constituents. Mr. Moore also discussed the effect of grain size. Mr. A. R. G. Brown discussed the importance of the variation of S-curves with composition, and the difficulties involved in determining the curves for fast-transforming steels. The effect of slow-cooling to the temperature of isothermal transformation was discussed by Dr. T. Ko, who illustrated his remarks with a number of examples. On the practical aspects, Mr. F. D. Waterfall considered that the Atlas was of more use in practical heat treatment than the authors had stated. He believed that further information would be welcomed on the effect of bar size, and on the diagrams for case-hardening and tool steels.

THE TRANSFORMATIONS $\alpha \rightarrow \gamma$ AND $\gamma \rightarrow \alpha$ IN IRON-RICH BINARY IRON-NICKEL ALLOYS*

By N. P. Allen and C. C. Earley

The work described in this paper has been carried out to determine the effect of nickel on the rate and mode of transformation in iron-nickel alloys, and forms part of a wider study of the effect of nickel on the transformation in iron. Iron and nickel form two solid solutions, α and γ, with body- and face-centred cubic structures respectively, and over a wide range of compositions and temperatures alloys in true equilibrium consist of a mixture of the two solid solutions. The α–phase formed on continuous cooling is a supersaturated solution containing the same proportion of nickel as the γ–phase from which it is formed: it is generally known as the α_2–phase. Alloys initially in the γ–state, when cooled to, and held at, temperatures within the $\alpha+\gamma$ field, show no evidence

* *J.I.S.I.* December, 1951

of transforming isothermally, whereas alloys initially in the α_2–state will transform at constant temperature if heated to a temperature close to the temperature of the spontaneous phase change $\alpha \rightarrow \gamma$ on continuous heating. During the isothermal transformation $\alpha \rightarrow \gamma$, α_2–phase decomposes into two other solid solutions of different nickel contents.

Dilatometric studies of the $\alpha_2 \rightarrow \alpha + \gamma$ transformation show that, according to composition and transformation temperature, two types of dilatation curves are obtained. In the first, there is a rapid initial contraction, i.e., a rapid phase change, without an induction period, followed by slow transformation, whilst the second type show a slow phase change with an induction period. Examination of the structures of specimens showing the first type of dilatation curve reveals a microscopically duplex structure consisting of an α_2–type of structure and a microscopically duplex structure whose phases are the α of the equilibrium composition and α_2 resulting from spontaneous decomposition of the γ of the equilibrium composition as the alloys are cooled to room temperature.

The kinetics of the slow isothermal transformation are discussed on the basis of a nucleation and growth mechanism, the velocity being assumed to be governed by the probability of the appearance of nuclei containing some 300 atoms.

Discussion

The discussion was opened by Dr. K. Hoselitz, who commented on the excellence of the experimental work, particularly of the metallography. On one point, he questioned the metallographic evidence, where about 6% nickel-rich α_2 is shown when 25% would be expected. Dr. Hoselitz also asked whether the authors had any explanation to offer for the quantitative disagreement between their work and the equilibrium diagram they had accepted as a basis.

Mr. E. H. Bucknall thought the authors had put their finger on the essential difference between martensitic and isothermal transformations over a wide field. It should be borne in mind, however, that they were dealing with a substitutional solid solution, instead of the interstitial type common in steels. It did not seem likely that there would be any difference in cases where separation of a phase which was not very high in solute content occurred, but very large differences were possible when phases rich in solute were concerned.

On the estimation of percentage of phases present, by metallographic methods, Mr. C. C. Earley, in reply, pointed out the importance of remembering that a microspecimen is only a section through a three dimensional material. One of the difficulties in work on the iron-nickel system concerned the slowness of diffusion which was responsible for variations in the equilibrium diagram.

THE ACCELERATION OF THE RATE OF ISOTHERMAL TRANSFORMATION OF AUSTENITE*

By M. D. Jepson and F. C. Thompson

The possibility of accelerating the rate of breakdown of austenite by means of thermal oscillations was considered on the grounds of the Thompson and Stanton stress-relief theory, since temperature fluctuations might assist the relief of internal stress. Experiments carried out on these lines resulted in a marked decrease in the transformation time being noted in the martensite range, most of the transformation occurring during the cooling part of the cycle.

The second part of the paper deals with the effect of stress on the rate of isothermal transformation, both tensile and compressive stresses being considered. Tensile stresses of the order of 10 tons/sq.in. are found to accelerate markedly the decomposition of austenite at constant temperature. Compressive stresses of a higher order seem to be necessary to produce a comparable effect, although there is no clear evidence to show that the effects are essentially different. Below a certain minimum stress, little or no acceleration occurs, and the increase in transformation rate increases with stress. Transformation under stress, to low temperature bainite, is marked by certain distributional effects, transformation taking place preferentially on slip or twin bands present in the parent austenite. Prolongation of the thermal and stress conditions, for a time far in excess of that required for complete transformation, results in a clarification of a granular structure and increased definition of the twin bands. This implies that some further change is taking place.

In explanation of these facts, it is suggested that the formation of low-temperature bainite is due to the combined action of shear and nucleation, the transformation being initiated by the former and continued as a result of the latter. The importance of the two effects varies with the temperature, nucleation being more important at higher temperatures and shear at lower temperatures. The effect of stress in the pearlitic range, including transformation to high-temperature bainite, is to produce, by deformation, extra nuclei of α–iron.

THE BREAKDOWN OF AUSTENITE BELOW THE M_s TEMPERATURE*

By F. C. Thompson and M. D. Jepson

After demonstrating that truly isothermal decomposition of austenite can be induced below the M_s temperature, even when the temperature is slowly rising, it is suggested that the decomposition during the actual quenching operation and that due to isothermal transformation should be considered independently, and so shown on the isothermal transformation diagram. The results of dilatometric investigations show that, so far as the second factor is concerned decomposition becomes progressively slower as the temperature is lowered, and that there is no sign of a knee in the curve. The nature of the transformation product in this range of temperature is considered, and it is concluded that martensite is first formed and subsequently tempered progressively with time, leading finally to an acicular bainitic product of secondary origin. Determinations of the maximum rate of breakdown suggest it is related to the temperature by an equation of the type $R_{max} = Ke^{x\theta}$. There appears to be a distinct break in the curve of temperature against maximum rate at the M_s temperature. The characteristic $\alpha\beta$ inversion of the martensite can be observed dilatometrically immediately after quenching, but it disappears as the isothermal treatment is prolonged and the martensite transforms.

The mechanism of the austenite-martensite transformation during isothermal treatment is discussed, and no reason is found to believe that it is not due to mechanical stress. Such stresses may be set up either in the martensite, through volume changes due to tempering, or by changes in the austenite. Diffusion, for instance,

* *J.I.S.I.* May, 1949.

* *J.I.S.I.* January, 1950.

might provide the explanation in the latter case, where, as magnetic results demonstrate, the austenite is by no means quiescent during the induction period.

Discussion

DR. L. B. PFEIL said he found it difficult to believe that, even in the absence of applied stress, the transformation of austenite at low temperatures was initiated by stress, nor could he accept the view that austenite, below the M_S point must transform to martensite and then be tempered to a baintic product. On the question of transformation below the M_S point, MR. C. E. MAVROCORDATOS was in agreement with Dr. Pfeil and queried the statement that "the product of isothermal transformation is due only to shear which has been initiated by stress" as, if that were so, the stress must be greater immediately after the formation of the "anisothermal" martensite. MR. E. H. BUCKNALL suggested that the hardness of the martensite found on cooling would be about 900 D.P.H. and that the transformation product of the residual austenite would be about 780 D.P.H. and temper slowly. The main difference between the isothermal product and martensite was that the former occurred as a result of nucleation and growth processes, whereas martensite had an almost infinite growth rate. MR. D. R. THORNEYCROFT commented that work he had carried out on En 40 B had shown the transformation below M_S to proceed according to continuation of the curves above M_S. He also referred to the metallographic similarity of tempered martensite and isothermal transformation products formed just above M_S.

PROFESSOR THOMPSON said the authors would make detailed comment on the discussion in writing.

News of the Month

New Coke Oven Plant

THE National Coal Board (Durham Division) have placed an order with The Woodall-Duckham Vertical Retort & Oven Construction Co. (1920) Ltd., for the design and erection of a comprehensive Coke Oven and By-Product Recovery Plant to be built at Fishburn Colliery, Co. Durham. The plant which incorporates many modern features will cost approximately £1,500,000 and is designed to carbonise 1,000 tons of coal per day. It comprises fifty W–D Becker Combination Underjet type Coke Ovens with appropriate oven machinery, coal blending, storage and service bunkers; coke handling, screening and storage bunkers, and full by-product recovery equipment for the production of crude tar, sulphate of ammonia and crude benzole. The contract includes the civil engineering work associated with the plant, water cooling and re-circulation services, and the construction of extensive railway sidings. Arrangements are being made by the National Coal Board for the disposal of the coke oven gas to the Northern Gas Board.

New Toolroom Tempering Furnaces

DESIGNED for low temperature heat-treatment two toolroom tempering furnaces, TRT.1010 and TRT.1020, rated at 4 kW and 8 kW respectively, are claimed to meet adequately the demands of the average toolroom. Manufactured by Wild-Barfield Electric Furnaces, Ltd., Elecfurn Works, Watford By-Pass, Watford, Herts., each model is of simplified design and construction yet embodying the recognised features of the larger production models.

The vigorous air circulation necessary to give a high degree of temperature uniformity throughout the charge space is assured by the centrifugal fan incorporated in their design. Precision of control as well as rapidity of heating are features not to be overlooked by those desiring a complete equipment which occupies the minimum of floor space. Rapid initial heating with close temperature control is effected by a switch by means of which one section of the heating elements may be cut out. Thus, by reducing the input, exceptionally close temperature control, even at temperatures as low as 175° C. (347° F.), makes it possible for expensive dies, press tools and milling cutters to be treated without risk of damage.

Designed primarily for tempering carbon, alloy and high speed steel tools, they are used for production purposes where the production lends itself to the use of a number of small individual furnaces.

British Welding Electrodes to be Manufactured in Australia

THE Board of Murex, Ltd., of Rainham, Essex, announce that, in conjunction with Australian Associates, they have participated in the formation of a new Company known as Murex (Australasia) Pty., Ltd. This Company has been formed primarily for the manufacture and sale of Murex Arc Welding Electrodes and Equipment, and will employ the most modern electrode manufacturing plant and techniques, with the full resources of the extensive Murex research organisation in England to assist its future development.

The Head Office of the new Company, with a modern factory and research department, is to be situated at Derwent Park, Hobart, Tasmania. Branch Offices are to be established in all Australian State capitals, and will later be extended to New Zealand. The Board of Directors consists of Messrs. Francis H. Foster, C. P. Flockart and D. E. Hopkins. The General Manager of the Company is Mr. Wilfred T. Bennett. Mr. E. J. Clarke, Director and Development Engineer of Murex Welding Processes, Ltd., is in Tasmania to advise on the installation and operation of the new manufacturing plant.

High-temperature Materials Symposium

Arrangements have now been made for the Fifth Hatfield Memorial Lecture to be delivered by Sir Frank Whittle on Tuesday, February 20th, 1951, preceding the Symposium on High-Temperature Steels and Alloys for Gas Turbines, which will take place on Wednesday and Thursday, February 21st and 22nd, 1951. Interested readers should get in touch with the Secretary of the Institute who will forward to them copies of the Circular giving details of the meetings, together with a Reply Form for their use.

Patents Covering Martempering

OVER twelve years ago Richard F. Harvey, who is now employed as a Metallurgist by Brown & Sharpe Manufacturing Co., Providence, R.I., developed a new hardening treatment which was first called "Step-Quenching" and later became known as "Martemper-

ing." Briefly, the method involves quenching from the austenitic temperature into a hot bath maintained above the temperature of martensite formation so that the cooling is interrupted. After attaining the temperature of the bath the parts are cooled slowly to room temperature. This avoids undesirable stresses, and results in less distortion and cracking than conventional quench methods.

A U.S. patent application, No. 320,998 filed on Feb. 27, 1940, covering this treatment, was eventually disallowed by the Patent Office. Subsequently, in the same year, a thesis on Step-Quenching was conducted at the Worcester Polytechnic Institute at Harvey's suggestion. It is noteworthy, therefore, that two Congressional Bills have been recently filed on Harvey's behalf to assist him in obtaining a patent on this heat treatment process.

Royal Society Awards

Sir Edward Appleton, G.B.E., K.C.B., F.R.S. and Dr. C. F. A. Pantin, F.R.S., have been awarded Royal Society Medals; Sir Edward for his work on the transmission of electromagnetic waves round the earth and for his investigations of the ionic state of the upper atmosphere and Dr. Pantin for his contributions to the comparative physiology of the Invertebrata, particularly his work on nerve conduction in Crustacea and Actinozoa.

Awards of Medals by the President and the Council of the Royal Society include :—

The Copley Medal to Sir James Chadwick, F.R.S., for his outstanding work in nuclear physics and in the development of atomic energy, especially for his discovery of the neutron.

The Rumford Medal to Air Commodore Sir Frank Whittle, K.B.E., C.B., F.R.S., for his pioneering contributions to the jet propulsion of aircraft.

The Davy Medal to Sir John Simonsen, F.R.S., for his distinguished researches on the constitution of natural products, especially the plant hydrocarbons and their derivatives.

The Darwin Medal to Professor F. E. Fritsch, F.R.S., for his distinguished contributions to the study of algology.

The Hughes Medal to Professor M. Born, F.R.S., for his contributions to theoretical physics in general and to the development of quantum mechanics in particular.

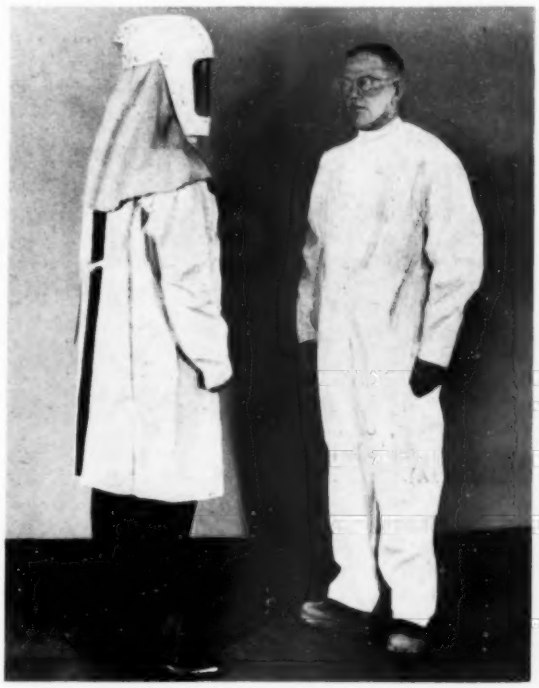
Proposed New Non-ferrous Metal Works for New Zealand

McKechnie Brothers, Ltd., the non-ferrous metal manufacturers of Rotten Park Street, Birmingham 16, are forming a Company in New Zealand under the title of McKechnie Brothers (N.Z.) Ltd., with a capital of £200,000 for the production of extruded brass, bronze, whitemetal and copper rods and sections, chill cast phosphor bronze bars, hot brass and bronze stampings, antifriction metal and other non-ferrous metal ingots. A plot of land in New Plymouth for the new works and part of the plant have already been purchased; plans are being prepared, and building operations should commence early in 1951.

The new Company should be in production in about 12 months and should be able to supply the whole of the Dominion's requirements for extruded brass and bronze rods and sections for some years to come. First directors will be Mr. W. Hayes (Managing) of the Birmingham Works, and Messrs. P. J. Ayckbourn and C. H. Wynyard of New Plymouth, New Zealand.

Comfortable Chemical-proof Clothing

The development of chemical-proof clothing which could be worn for long periods without discomfort has been occupying the attention of the Protective Industrial Clothing Division of the R.F.D. Company for the past two years. The result is clothing employing a new lightweight material, new styles and a new method of seaming.



The material is high-grade cotton cloth proofed both sides with white P.V.C. (Polyvinyl-chloride) to R.F.D. specification. It weighs only 8½ oz./sq.yd. and is extremely flexible and resistant to abrasion and tearing. It is impervious to most chemicals, including acids, alkalis, oils and greases, and such miscellaneous chemicals as aluminium chloride and hydrogen peroxide. It is simplicity itself to keep clean with the aid of a damp cloth.

The garments available include bib and brace overalls, bib aprons, jumpers, hoods, surgeon's type coats, trousers, wader type trousers, combination suits and laboratory coats. Special attention has been paid to ventilation and freedom of movement and extra comfort is provided by gusset type sleeves and trouser legs, with two position adjustment for wearing over or under gloves or gum boots.

Plain stitched seams permit chemical penetration, while both thermal and plastic seams lack the strength of sewn seams. To meet this difficulty, the seams are first doubly sewn for strength and then sealed with a specially formulated chemical film, which has exactly the same properties and resistance to abrasion as the material itself. *R.F.D. Co. Ltd., Godalming, Surrey.*

The Influence of Surface Contamination on the Corrosion of Magnesium Manganese Sheet*

By L. Rakowski, Inz. Chem. (Warsaw)†

Surface contamination greatly reduces the corrosion resistance of chromate treated magnesium manganese sheet towards seawater spray. The contamination is revealed by chromate treatment in the hot half-hour bath (bath iii of D.T.D. 911A); it may be general in nature, leading to poor streaky chromate films, or it may take the form of small white spots of metal which do not treat. The latter type has been shown to consist of small particles of foreign metals embedded in the surface. Cleaning methods are described which remove both types of contamination so that good corrosion resistance is obtained.

MAGNESIUM manganese sheet containing 98·5% Mg and 1·5% Mn (known as AM 503 and complying with Ministry of Supply Specification D.T.D.118) was widely used in military aircraft during the war. For protection during storage and transit, it is usual for the manufacturer to treat the sheet in the I.G. acid chromate dip (20% nitric acid, 15% sodium dichromate bath iv of D.T.D.911A) and then apply a coating of lanolin. After fabrication, the sheet is degreased and chromate treated again, either in the acid chromate dip again, or in the hot half-hour chromate bath (bath iii of D.T.D.911A). This latter bath consists of a solution of 1·5% sodium dichromate, 1·5% ammonium dichromate, 3·0% ammonium sulphate and about 0·4% ammonia solution (Sp. Gr. 0·880), sufficient to bring the *p*H to 6·1. Magnesium manganese sheet immersed for half an hour in the boiling bath solution should become coated with a uniform straw-brown film.

Difficulty in obtaining a uniform protective film during retreatment in the hot half-hour bath was sometimes encountered and an investigation has been made into the cause and into methods of overcoming it. Poor treatments were found to fall into two classes: (*a*) films which were streaky and of a grey or grey-brown colour instead of uniform straw-brown, and (*b*) films which were uniform straw-brown but which contained white spots of untreated metal.

* Based on the original paper in Metaux et Corrosion. Vol. XXIV, No. 289, September, 1949.

† Late of Metallurgy Department, Royal Aircraft Establishment, Farnborough, now of Research Department, Messrs. Courtaulds Ltd., Coventry.

Sheet Giving Streaky Films

General Surface Contamination

The appearance of magnesium manganese sheet giving a poor streaky chromate film is shown in the left hand side of Fig. 1. It was found that good films could be produced on such material if the surface layers were removed by repeated rubbing with an abrasive powder such as pumice powder, or by immersion in a 10% solution of

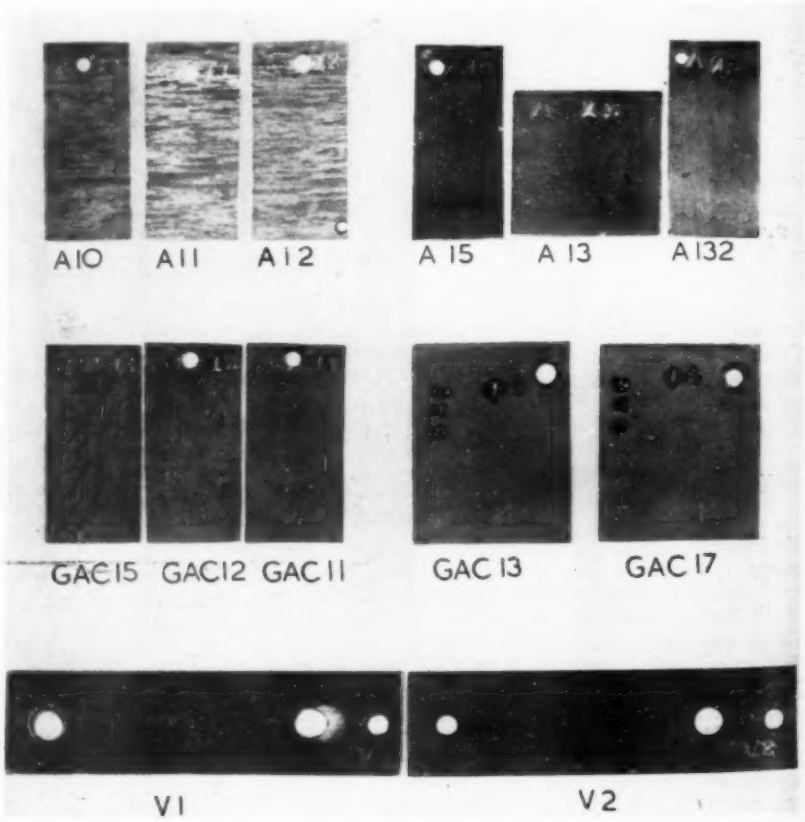


Fig. 1.– Appearance of specimens chromated in bath iii of D.T.D. 911 after various cleaning treatments.

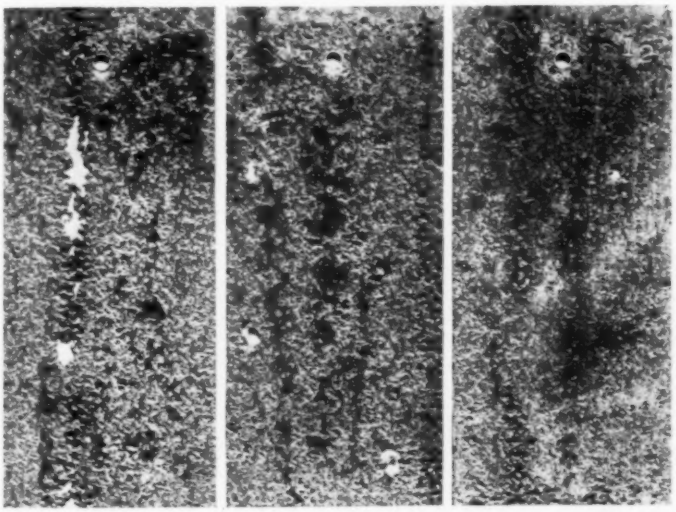
caustic soda followed by immersion in mineral acid, e.g., 5% nitric acid. The appearance of the chromate film on sheets cleaned in this way is shown on the right hand side of Fig. 1.

The contamination varied in degree with the three sheets illustrated in Fig. 1. For example, sheets G.A.C. and V were sufficiently cleaned by light rubbing with wet pumice powder or by a short pickle in 5% nitric acid. The contamination on sheet A, however, was so great that very considerable removal of metal surface was necessary before a good chromate film could be produced. The harmful effect of streaks of this type on corrosion resistance is shown in Fig. 2.

It seems likely that this type of contamination is due to carbonaceous products from the lubricant used during the rolling of the sheet, or possibly to flux inclusions in the billet.

A second type of streakiness has also been observed to develop on some apparently uniform specimens after exposure to the intermittent seawater spray test. The phenomenon, illustrated in Fig. 3, consists of elongated areas of uncorroded metal. Such streaks are probably caused by local cold work produced during straightening operations; it has been often noticed that edges and stamp marks on magnesium manganese sheet corrode less than the rest of the specimen.

Fig. 2.—Appearance of specimens originally exhibiting streaky chromate films after seawater spray corrosion test.



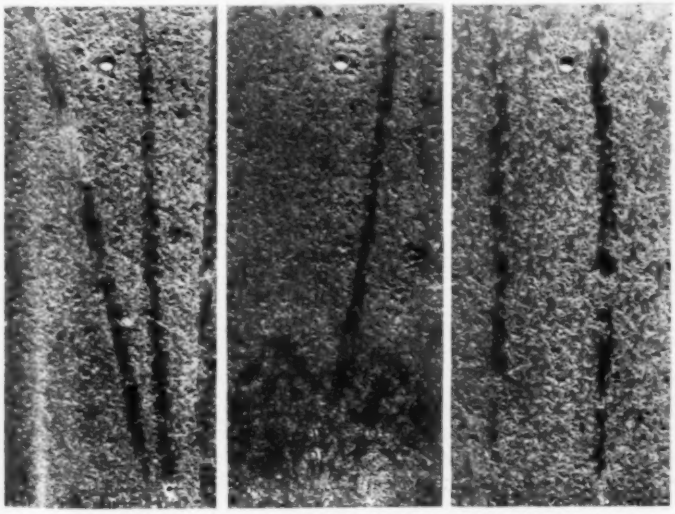


Fig. 3.—Streaks of uncorroded metal showing after seawater spray test on specimens having normal chromate films. Local cold work is probably responsible for this phenomenon.

Sheet Giving Untreated Spots

Local Contamination

The appearance of this type of sheet after chromate treatment in the hot half-hour bath is shown in the left hand side of Fig. 4. A photographic enlargement of the white spots is also shown. On exposure to the R.A.E. intermittent seawater spray test intense local corrosion developed round the white spots, leading eventually to perforation of the sheet, as shown in Fig. 4. The remaining areas of the sheet were substantially unattacked. Perforation of this type often took place in the form of a ring round the centre of the white spot

It seemed likely that this type of contamination was due to metallic inclusions impressed into the surface of the sheet during rolling or fabrication. This was shown to be so for the two specimens illustrated in Fig. 4. Electrographic surface prints made by the method described by Hunter et al.[1] showed that the spot on specimen 2EF14 was an iron particle, and that on 3ER17 a copper particle. The "tailing" effect shown in Fig. 4 indicates that the inclusions acted a cathodes during chromate treatment. Caustic soda produced at the inclusion locally raises the *p*H value sufficiently to prevent the formation of chromate film. The alkaline area is swept upwards by the stream of hydrogen bubbles also liberated at the cathode.

Methods of Cleaning Contaminated Sheet

Although it was clear that the best way of obtaining good corrosion resistance on magnesium manganese sheet was to avoid contamination of all kinds, it was thought advisable to investigate practical methods of cleaning sheet which had become contaminated.

Three sheets were selected for the experiments; the compositions by analysis were as follows :—

Sheet No.	Percentage Composition							
	Al	Zn	Mn	Fe	Cu	Ni	Si	Mg
X	None	0·01	1·51	0·03	0·01	None	None	Rem.
2E	Trace	None	1·51	0·017	0·01	None	None	Rem.
1V	0·18	0·02	1·49	0·02	0·01	0·005	None	Rem.

Sheet X showed the first type of contamination and gave poor streaky films, the streaks being in the direction of rolling. Sheets 2E and 1V showed the second type, giving good uniform films but containing white spots due to metallic inclusions. All three sheets had been treated in the acid chromate dip and then coated with lanolin.

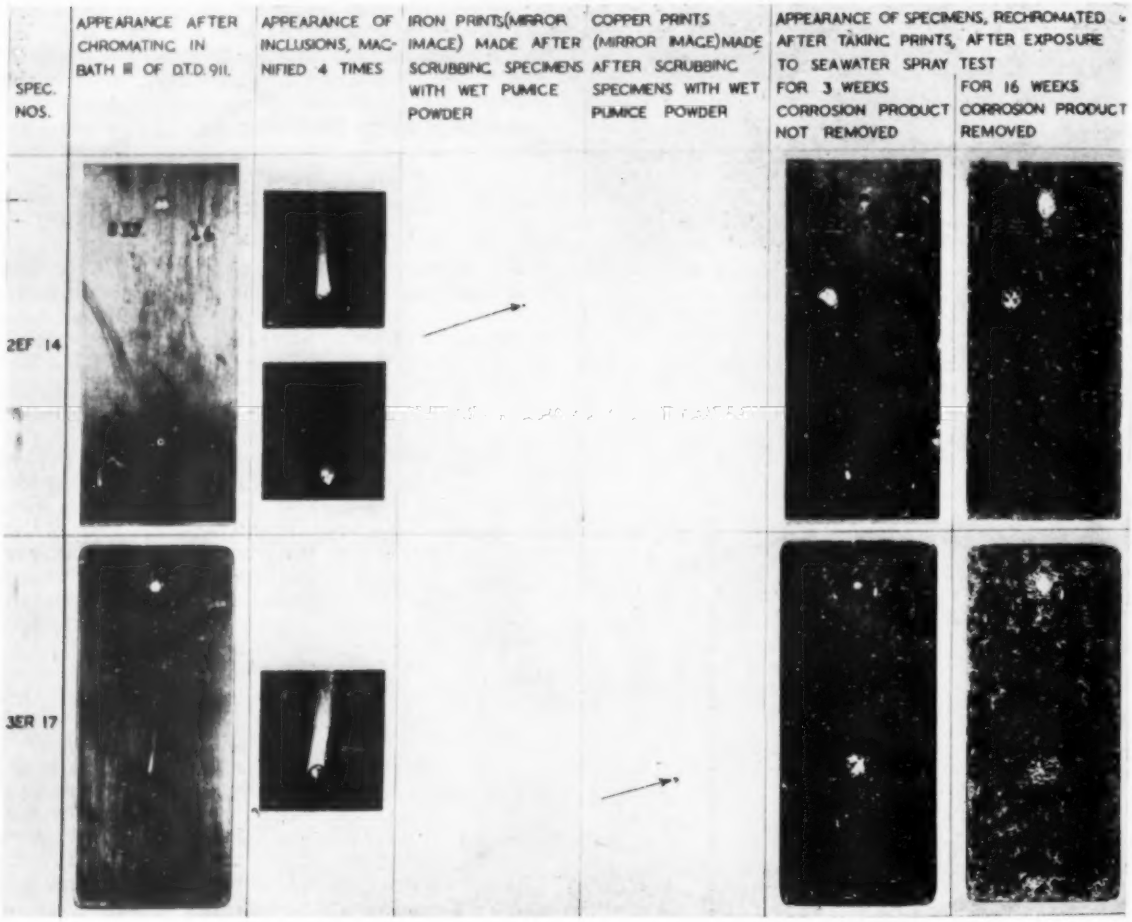

SPEC. NOS.
APPEARANCE AFTER CHROMATING IN BATH III OF D.T.D. 911.
APPEARANCE OF INCLUSIONS, MAGNIFIED 4 TIMES
IRON PRINTS (MIRROR IMAGE) MADE AFTER SCRUBBING SPECIMENS WITH WET PUMICE POWDER
COPPER PRINTS (MIRROR IMAGE) MADE AFTER SCRUBBING SPECIMENS WITH WET PUMICE POWDER
APPEARANCE OF SPECIMENS, RECHROMATED AFTER TAKING PRINTS, AFTER EXPOSURE TO SEAWATER SPRAY TEST
FOR 3 WEEKS CORROSION PRODUCT NOT REMOVED
FOR 16 WEEKS CORROSION PRODUCT REMOVED
2EF 14
3ER 17

Fig. 4.—Effect of metallic inclusions on localised corrosion of chromate-treated D.T.D. 118 magnesium alloy sheet.

Quadruplicate sets of specimens each of surface area 1 sq. dm. were selected in such a way as to eliminate any systematic change in intrinsic corrosion resistance along the length of the sheet[2]. The specimens were degreased in trichlorethylene vapour and before re-treatment in the hot half-hour chromate bath they were cleaned by one or other of the following treatments :—

(1) Immersion for 15 minutes in a boiling 5% aqueous solution of an alkaline metal cleaner. This may be considered as the standard method of cleaning. The treatment modifies the acid chromate dip film but does not remove it.

(2) The acid chromate dip film was removed by abrasion with wet pumice powder. No further cleaning was given.

(3) Combination of 2 and 1, pumice powder followed by immersion in the alkaline metal cleaner.

(4) Immersion for 15 minutes in a boiling 5% solution of caustic soda followed by a 40 seconds' pickle in 5% nitric acid. The caustic soda substantially modifies the acid chromate dip film; what remains is readily removed by nitric acid to leave a bright surface.

(5) Immersion in boiling caustic soda solution as in No. 4 followed by immersion for 15 seconds in a cold solution of 10% nitric acid saturated with magnesium nitrate.

(6) Immersion for 10 minutes in the nitrobenzene/fuming nitric acid mixture. This mixture (B.P. 499,046, L. F. Le Brocq and H. Sutton) consists of 100 parts by volume of nitrobenzene, 10 parts of fuming nitric acid (Sp. Gr. 1·5) and 2 to 3 parts of water. The water is added until it forms a slight permanent second phase in the form of aqueous nitric acid which sinks to the bottom of the mixture. Without water, the solvent action of the bath is very sluggish. Magnesium alloy parts must not, of course, be allowed to come in contact with the aqueous layer on the bottom. The mixture removes previous chromate film with little attack on the metal. The surface of the metal is left dull in appearance.

(7) As No. 6, followed by a 15 seconds' pickle in 5% nitric acid to brighten the surface.

(8) Immersion in boiling 5% caustic soda, followed by immersion for 10 minutes in boiling 10% chromic acid (CrO_3) solution. This reagent has been used to remove corrosion product from magnesium

TABLE I.—SEAWATER SPRAY CORROSION TESTS ON MAGNESIUM MANGANESE SHEET CLEANED BY VARIOUS SPECIAL METHODS AND THEN CHROMATE TREATED IN BATHS III OR IV OF SPECIFICATION D.T.D. 911A.

The specimens had originally been treated in the acid chromate dip (bath iv) and then coated with lanolin. The specimens were degreased in trichlorethylene vapour before applying the cleaning treatments described, followed by final chromate treatment.
Period of exposure: Sheet X—2 months; Sheets 2B and 1V—6 months.

Scheme No.	Cleaning agents	Metal removed (g./sq. dm.) from sheet bearing film from :—		Appearance of metal after cleaning treatment	Final chromate treatment	Appearance after chromate treatment			Streaky sheet X		Sheets 2E and 1V with inclusions				Mean order of merit
											2E		1V		
		Bath iii	Bath iv			Sheet X	Sheet 2E	Sheet 1V	Mean corrosion loss g./sq. dm.	Order of merit	Mean corrosion loss g./sq. dm.	Order of merit	Mean corrosion loss g./sq. dm.	Order of merit	
1	5% alkaline metal cleaner	None	None	Mat gr.grn.	Bath iii	Poor	Good	Good	1·09	11	1·96	12	0·60	13	13
3	Pumice, then alkaline cleaner	0·054	0·020	Bright	,,	,,	,,	,,	1·00	10	0·76	11	0·54	12	11
3a	Pumice, alkaline cleaner bath iii, three times in all	0·402	0·368	,,	,,	Good	,,	,,	0·50	5	0·13	3	0·23	8	5
4	5% NaOH, 5% HNO_3..	0·296	0·229	,,	,,	,,	,,	,,	0·34	3	0·53	10	0·24	9	9
5	5% NaOH, 10% HNO_3, sat. $Mg(NO_3)_2$	0·085	0·073	,,	,,	,,	,,	,,	0·50	6	0·91	13	0·25	10	11
6	Nitrobenzene/nitric acid	0·035	0·029	Dull grey	,,	—	Fair	Fair	—	—	0·14	5	0·11	3	3
7	Nitrobenzene/nitric acid, 5% HNO_3 ..	0·089	0·074	Bright	,,	—	Good	Good	—	—	0·30	8	0·32	11	9
8	5% NaOH, 10% CrO_3, 5% NaOH	None	None	Slightly mat	,,	Fair	Fair	Fair	0·17	1	0·26	7	0·14	4	5
9	5% NaOH, 10% CrO_3, 2 % HF	0·010	0·010	,, ,,	,,	Good	Good	,,	0·24	2	0·13	4	0·18	6	4
10	5% NaOH, 10% CrO_3, sat. NaF, HF/HNO_3	0·005	0·005	,, ,,	,,	Poor	,,	Good	0·37	4	0·08	1	0·10	2	1
11	5% NaOH, sat. NaF, HF/HNO_3	None	None	Bright	,,	,,	,,	,,	0·70	8	0·12	2	0·10	1	1
12	5% NaOH, bath iv, HF/HNO_3	0·090	0·090	,,	,,	Good	,,	,,	0·72	9	0·15	6	0·23	7	7
13	Pumice, NaCN, alkaline cleaner	0·054	0·020	,,	,,	Poor	,,	,,	1·11	12	0·45	9	0·15	5	8
2	Rubbed with wet pumice powder ..	0·054	0·020	Bright	Bath iv	Good	Good	Good	0·37	2	2·26	4	0·39	3	4
8	5% NaOH, 10% CrO_3, 5% NaOH	None	None	Slightly mat	,,	,,	,,	,,	0·26	1	1·30	3	0·29	1	2
11	5% NaOH, sat. NaF, HF/HNO_3	,,	,,	Bright	,,	—	,,	,,	—	—	0·88	1	0·30	2	1
12	5% NaOH, Bath iv, HF/HNO_3	0·090	0·090	,,	,,	—	,,	,,	—	—	0·88	1	0·58	4	3

alloys without attack on the metal; the metal surface is, however, left in a passivated condition, and accordingly the specimens were again immersed in boiling 5% caustic soda before re-chromate treatment.

(9) Immersion in caustic soda, then in chromic acid as in No. 8, followed by 5 minutes' immersion in cold 20% hydrofluoric acid (HF) solution. This solution has only a slight solvent action on magnesium alloys but has a strong solvent effect on any iron or aluminium alloy inclusions.

(10) Immersion in caustic soda, then in chromic acid as in Nos. 8 and 9, followed by dipping into a saturated solution of sodium fluoride and immersion for 10 minutes in a solution containing 2 parts by volume of 40% hydrofluoric acid and 1 part by volume of nitric acid (Sp. Gr. 1·42). This solution (B.P. 589,932, L. Rakowski) attacks iron, nickel, copper and aluminium, but does not attack magnesium alloys appreciably. If the solution is diluted, however, it will attack magnesium alloys vigorously. The specimens, therefore, should first be dried or should be dipped in strong sodium fluoride solution.

(11) Immersion in caustic soda, followed by dipping in sodium fluoride and immersion in the hydrofluoric acid/nitric acid mixture, i.e., as No. 10 but without the chromic acid immersion.

(12) Immersion in caustic soda, followed by treatment in the acid chromate dip (used as a cleaning treatment here), then immersion in the hydrofluoric acid/nitric acid mixture.

(13) Abrasion with wet pumice powder, then immersion for 2 hours in a cold 10% sodium cyanide solution through which a stream of air was bubbled, followed by immersion in the boiling alkaline metal cleaning solution. It was hoped that the sodium cyanide would dissolve embedded iron or copper particles.

The appearance of the cleaned specimens is given in Table I, together with figures for the loss of metal, as g./sq. dm., caused by the cleaning treatment.

The cleaned specimens were then chromate treated in the hot half-hour chromate bath, or in some cases in the acid chromate dip. The appearance of the treated specimens is given in the Table.

Corrosion Tests

The chromate treated specimens were then exposed to the R.A.E. intermittent seawater spray test. In this test the specimens are hung by glass hooks from glass rods in a covered shed open to the air on one side. The specimens are sprayed three times a day with seawater from the English Channel. The periods of exposure are given in Table I.

After exposure, the specimens were washed free from gross corrosion product and then immersed overnight in a cold 10% solution of ammonium chromate through which a stream of air was bubbled. This treatment[3] removes corrosion product without appreciable attack on metal or chromate film. The cleaned and dried specimens were weighed and the losses of weight of metal due to corrosion were calculated as g./sq. dm. The mean losses in weight are quoted in the Table.

Discussion of Results

The results of the corrosion tests, together with orders of merit of the cleaning treatments, are given in Table I.

Considering the specimens treated in the hot half-hour bath (bath iii), it will be seen that the corrosion resistance of sheet X, which suffered from general contamination, was greatly improved by cleaning treatments 8, 9 and 10, each of which included an immersion in boiling chromic acid solution, and by treatment 4 (caustic soda followed by nitric acid). Treatments 8, 9 or 10 are recommended where appreciable loss of metal must be avoided; treatment 4 is a quick simple treatment recommended where loss of metal is not so important.

The corrosion resistance of sheets 2E and 1V, which contained metallic inclusions in the surface, was greatly improved by treatments 10 and 11, both of which included an immersion in the hydrofluoric acid/nitric acid mixture which dissolves the inclusions. Immersion in nitrobenzene/nitric acid (No. 6) and the treatments including chromic acid (Nos. 8 and 9) also gave good results.

Special cleaning methods also gave improved protection to specimens treated in the acid chromate dip (bath iv); the improvement was not, however, so great as when the hot half-hour bath (bath iii) was used. It seems that the hot bath gives the greater protection provided that the metal surface is clean, whether by careful manufacture or as a result of subsequent cleaning treatment. Where no precautions have been taken to avoid contamination, however, the acid dip gives the better results, since it has in itself considerable cleaning action.

Conclusions

Surface contamination greatly reduces the corrosion resistance of magnesium manganese sheet towards seawater spray. The contamination may be general or may be in the form of local inclusion of foreign metals, and is revealed on chromate treatment in the hot half-hour bath (bath iii of D.T.D.911A).

Cleaning methods designed to remove the contamination lead to greatly improved corrosion resistance.

Acknowledgments

The author wishes to thank the Ministry of Supply for permission to publish the results of this work. No responsibility attaches to the Ministry for any expression of opinion in this paper, the opinions being the responsibility of the author.

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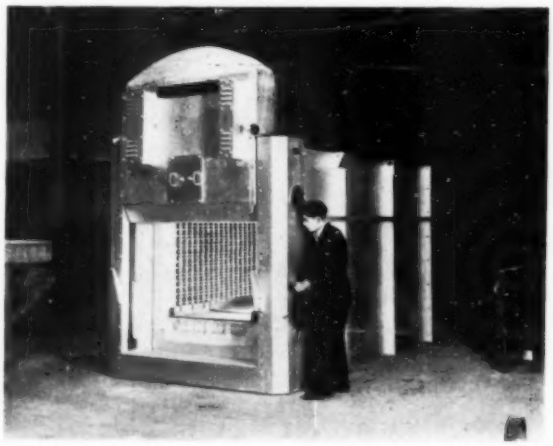
1 Hunter, Churchill and Mears. Electrographic methods of Surface Analysis. *Metal Progress*, December, 1942.
2 Jones and Mrs. Petch. Variations in corrosion properties over Magnesium alloy sheets. *J. Inst. Metals*, 73, Part 3, p. 129 (1946).
3 Private Communication from L. F. Le Brocq, R.A.E., Farnborough.

Furnace for South Africa

A HEAVY Hairpin batch type electric furnace recently exported to South Africa is reported to be the largest electric furnace to be imported by that country as a complete unit ready for operation, up to the present time. The heating chamber is 8 ft. long, 3 ft. wide and 3 ft. high. It is a high temperature multi-purpose unit with an operating temperature range between 300° and 1,000° C. A total rating of 110 kW has been supplied, this being a single zone controlled by a combined recording and controlling instrument. To cut down current consumption on low temperature processes and those requiring lengthy soaking times, a Star Delta switch is incorporated to reduce the normal rating of the unit to one-third. The furnace is to be used in the workshops of the City of Durban Transport Department for the hardening and tempering of leaf springs, preheating of cylinder blocks and crank cases prior to welding and the annealing of cylinder blocks and crank cases after welding.

A special feature is the ease of removing the elements while the furnace is at temperature. Removal being effected from the front of the unit after the elements have been disconnected at the rear. Specially moulded open-type element firebricks permit a high degree of heat radiation while efficiently supporting the elements and permitting easy withdrawal and insertion. The hearth is covered with heavy heat-resisting alloy plates, which both protect the brickwork and support the charge. Full allowance is made for thermal expansion of these plates, for this reason they are in sections.

As will be noted from the accompanying illustration the furnace is of modern design, all the working parts of the door, for instance, are totally enclosed. This design also cuts down to a minimum the headroom required by



the unit; balance weights ride up and down at the rear of the unit connected to the door by means of roller chains running along the top of the roof. An 8 in. square aperture with a removable plug is fitted in the door to accommodate extra long omnibus springs. The unit was made by G. W. B. Electric Furnaces, Ltd.

Spheroidal-Graphite Cast Iron

THE first Conference of the British manufacturers of magnesium-treated spheroidal-graphite cast iron, licensed by The Mond Nickel Co., was held in Birmingham recently. Nineteen representatives of seven licensees joined in technical discussions, under the Chairmanship of Dr. L. B. Pfeil, and afterwards visited the Research Laboratory of The Mond Nickel Company, Limited.

Recent Progress in the Production and Fabrication of Stainless Steels

With Particular Reference to Sheet and Strip

Progress in the production of stainless sheet and strip steel is making considerable headway to meet the growing demands during recent years. Attention is being given to the production of wide strip in all the recognised types of surface finish. Fabricating techniques have also been developed which enable operations to be carried out on, more particularly, the austenitic stainless steels, with which this article is mainly concerned. Brief reference is also made to some recently developed heat-resisting alloys.

THE difficulty of obtaining an adequate supply of stainless steel since the war has been a considerable source of worry to many fabricators, and the problem of distributing the qualities available, a headache to the manufacturers. This problem has been particularly acute where stainless steel has been required in the form of sheet, as the demand has grown so rapidly in the last few years. The largest British producer of these special alloy steels is Firth-Vickers Stainless Steels, Ltd., of Sheffield, a considerable proportion of their output being in the form of sheet and strip, which is supplied in all the recognised types of surface finish, from descaled or pickled to a bright mirror polish.

Up to the present time the common practice in this country for producing stainless steel sheets has been by means of the conventional pull-over mills, but towards the end of the last war Firth-Vickers, who have always been in the forefront of development in the production of stainless steel, envisaged a new project for producing sheets from wide strip.

The new plant, which has the unique advantage of being designed for the sole purpose of handling stainless steel, will produce strip up to 1 metre wide in coil, for subsequent shearing into individual sheets or narrow strip. The original intention was not only to augment their sheet production but also to obtain certain improvements, particularly as regards surface finish, which were being obtained in America on their large continuous mills.

To gain the full benefit of bulk production so essential for the economical operation of such a factory, Samuel Fox & Co., Ltd., of Stocksbridge, have taken a one-third interest in this new plant so that in future it will supply both companies with sufficient strip to meet their combined requirements for the production of sheet from 10 gauge to 30 gauge in thickness, and up to 1 metre wide, in all the popular qualities.

The usual method of producing stainless steel sheet from an ingot, which may have been chipped or machined, is by roll-cogging to a slab. After grinding and cutting up, this is re-rolled to a sheet bar which is cut up into "moulds." Each individual mould is then dressed and hot-rolled into a sheet. With alloy steels of this nature it is necessary to free the surface from scale, either mechanically or chemically, after every hot operation, and also to soften the steel by heat-treatment, by reason of its work-hardening properties. During the hot-rolling this latter effect is covered by reheating during the process, but it will be seen that several cycles of treatment may be necessary during cold-rolling. With the new plant this practice will continue, but modern production will simplify the task with continuous processes. The plan shown in Fig. 1, illustrates the production flow.

Stainless steel slabs will be delivered into the slab preparation shop, where they will be dressed and cut into suitable lengths for hot-rolling. The slabs are then fed through a continuous gas furnace to be discharged directly on to the hot mill train. This comprises two hot mills which have been chosen after a complete study of the latest production methods in the United States. For the first reduction, the slabs pass through a two-high roughing mill followed by edging rolls, the finished thickness of hot-rolled strip being attained on a fast four-high mill, and passed straight into an up-coiler. In the beginning the length of these strips will be kept to approximately 70 ft. owing to limitations of temperature, but the four-high mill has been so designed that Steckel equipment can be added as the demand for the steel allows. This will enable the use of a much longer slab and, consequently, very much longer strip.

In order to cold-roll this strip economically, it is necessary to build the short coils into one long coil weighing from 3 to 5 tons. To do this a coil build-up line has been installed in which the coils are flash butt-welded together to produce a coil of the required weight for cold rolling. Service strips will also be welded on to the ends of the coils for passing round the coiler drums in the cold-rolling mills to minimise wastage of stainless steel.

Prior to cold-rolling, all the strip must be softened and descaled, so the hot-rolled coils from the build-up line are loaded into an uncoiler, passed through a roller flattening machine to a spot welder which fastens them to the preceding coil. There is a looping device after the welding which allows the strip to continue moving through the furnace although the end is stationary during the short period required to spot weld the next coil. It is absolutely essential that the strip should pass through the softening furnace at a controlled speed in view of the high temperature required for softening the austenitic qualities of stainless steel particularly, where thin gauge material is being treated.

The strip is cooled by air blast and moves in the same continuous line into the sodium hydride descaling bath, followed by a rinse tank. The strip then passes through a final acid bath after which it is washed with hot water, dried in hot air and passed over a second looping device which allows the strip to continue its movement whilst the spot weld is cut out. Each length of strip is then recoiled and transported to the cold-rolling mill. The softening furnaces burn town gas and are some 60 ft. long. During the initial heating the strip is supported

on rollers, after which it is allowed to hang in a free catenary curve in the hot chamber, although direct contact with the flame is avoided by an overtopped carborundum muffle.

Two cold-rolling mills are being installed for reducing the hot-rolled strip to the finished thickness. The first is a Robertson four-high reversing mill with work rolls of 17 in. diameter and backing rolls 49 in. diameter, and a drum coiler on either side of the mill. It can also be used as a straight-through mill by the provision of an upcoiler on the outgoing side. This latter arrangement will be in normal use as the mill will be required to reduce the hot-rolled strip to 0·080 in. thick although it will be capable of reducing strip to any desired gauge with the necessary intermediate softening and descaling treatment.

The second mill is particularly interesting, being of the Sendzimir cluster type which consists of two working rolls, each 2·125 in. diameter which are not driven, backed up by four intermediate rolls, these backed up by six further rolls, four of which are driven. A further eight backing rolls consist of a number of heavy roller bearings mounted on shafts which transmit the rolling load to the heavy cast steel housing through a number of cast steel saddles. To apply the rolling load the two upper backing rolls are mounted on an eccentric which is rotated by a rack and pinion driven from an hydraulic cylinder. This Sendzimir mill is particularly suitable for rolling the austenitic qualities of stainless steel which work harden rapidly, as the very small diameter work rolls enable greater reductions between softening treatments.

All coils of cold-rolled strip are passed through a rewinding line before leaving the department. This is necessitated by the fact that the very high coiling tensions are too great for collapsible drums, and solid steel drums have to be used. The rewinding line coils the strip on to a reel which can be collapsed, which also enables the service strips or " tails " to be removed and recoiled for further use. The strip is then passed through to the softening and descaling line.

When the coils have been rolled down to the finished gauge and finally softened and descaled they are passed to the warehouses of the two interested companies where the final finishing operations are carried out. In the Firth-Vickers warehouse, coils are passed to the cut-up line where they are unwound, flattened and re-sheared to the required sizes; subsequently they are inspected and tested before going to the despatch section.

It is anticipated that all this new plant will be in production by the end of 1951, and that sheets up to 1 metre wide will be rolled in the well-known " Staybrite " qualities. This will release much of the present rolling capacity for the production of wider sheets, and special qualities.

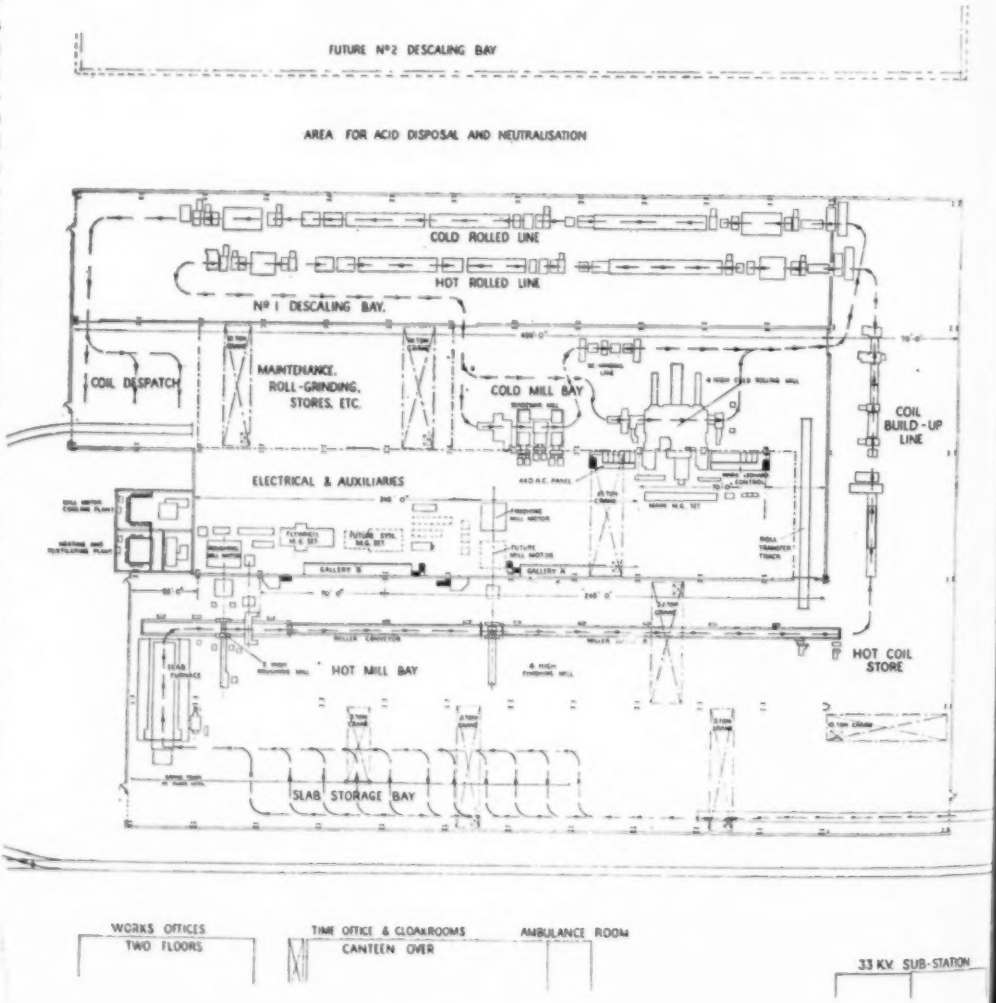


Fig. 1.—Layout of the buildings and plant.

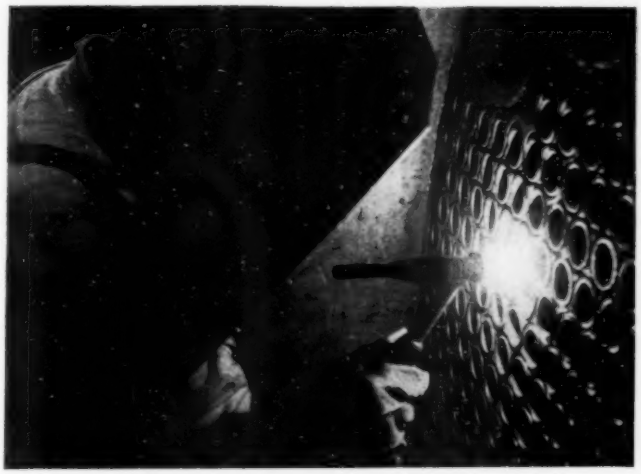


Fig. 2.—Welding "Staybrite" Steel by the argon arc method.

Sheets produced by Firth-Vickers, whether rolled by the new continuous method or on the present mills, will be normally available in the fully softened and descaled condition up to 10 ft. long.

The standard polished finishes that are already produced at Firth-Vickers Blackheath works will continue with the more up-to-date plant that has been introduced. The latest types of abrasive belt polishing and grinding machines of American manufacture have recently been acquired to improve production capacity and replace older machinery.

Qualities of Stainless Steel

As is well known, there are many qualities of "stainless" steel and this term in itself tends, sometimes, to be misleading as it embraces a large number of steels of widely differing compositions in order to provide suitable properties according to the particular job for which they are required. The range of qualities is given in Table I.

The austenitic stainless steels, classified by Firth-Vickers as "Staybrite" steels, are adaptable to a wide range of uses for which plain chromium stainless steels would not be satisfactory, and it is with the austenitic steels that this article is mainly concerned, although the new rolling capacity will also produce sheets in other specialised qualities.

It is important to remember that to obtain the full advantages and maximum corrosion resistance from these steels, full attention must be given to the proper heat-treatment, details of which are available and should be systematically followed if the ultimate consumer is to obtain the fullest benefit.

Similarly, in the machining of the "Staybrite" steels, the technique is different, not difficult, because by their very composition these steels are work hardening. It is essential that all tools should have a keen edge so that a true cutting action is obtained without rubbing, which latter causes work hardening to take place and increases the difficulty in cutting. This aspect has been covered very thoroughly and extensive tests with these special steels covering cutting rates, tools, lubricants, etc., have been carried out and form a guide to the correct procedure to be followed. It will be appreciated that machining conditions vary according to the dimensions of the particular component.

Fig. 3.—Flux injection flame cutting method for stainless steels.

It is of first importance to choose the quality of steel most suited to the service conditions, and where corrosion, in particular, is involved it is preferable to test qualities of steel under actual working conditions. Where this is not practicable, advantage can be taken of available data based on a wide range of trials and tests carried out over many years under a great variety of corroding conditions.

In dealing with these austenitic stainless steels it is advisable that all those concerned with their manipulation and fabrication should be as well informed on their difference from other metals as possible. Care should be taken with this material, bearing in mind the extra cost involved in its purchase.

Welding

The steels mentioned in Table I, with the exception of FST and DDQ, may be readily welded without subsequent heat-treatment. It is always advisable to use a recommended electrode (of type appropriate to the quality of steel being welded) and if the correct procedure is followed it is practicable to make welds which have the same corrosion resistance as the sheet or plate. The most recent development in the welding of "Staybrite" steel sheets and plates is the argon arc method (see Fig. 2). A tungsten electrode is used with either direct or alternating current plus a high frequency current. An annular stream of argon (which is a completely inert gas) envelops the arc and, as a result, oxidation of both the weld metal and the parent metal is very considerably reduced. This proves to be a great advantage as it reduces the finishing costs.

Flame Cutting

Another recent development which has been effected in connection with stainless steels is flame cutting (see Fig. 3). Machine cutting has always presented some difficulty to the fabricator, but to the steel manufacturer

these difficulties are increased by the thicker sections required to be cut. In general, machines designed for mild steel cutting can deal with stainless steel up to only 50% of their rated capacity, so that shears, guillotines and cold saws for exclusive use with stainless steel are initially more costly. In addition the work-hardening characteristics of these austenitic stainless steels demands the maintenance of a good cutting edge and as a direct result the running costs of such machinery tend to be very high.

The ease with which mild steel of varying thicknesses can be cut accurately with oxy-acetylene blow pipes has attracted attention, but the element chromium, which is present in considerable quantity in all stainless steels, resists the action of flame cutting by the formation of chromic oxide. Thin plates of stainless steel may be cut by normal oxy-acetylene methods but the action is entirely one of "melting away" and the cut is not completely controllable.

The advent of the flux injection flame cutting method in the United States showed a tremendous advance on all previous attempts to flame cut stainless steel. Briefly, the process consists of introducing a suitable flux in the form of a finely divided powder into the burning zone of an oxy-acetylene blow pipe. This powder provides a heavy dilution of the chromic oxide which keeps the slag fluid until blown clear of the cut.

Although experiments are still proceeding to discover an even more reliable method of introducing the powder into the blow pipe, the advantages already shown are so outstanding that Firth-Vickers have adopted the process as a standard procedure in cutting austenitic stainless steel slabs (from $2\frac{1}{2}$ in. to 5 in. thick). As a comparison, it has been found that whilst the cold sawing of a 14 in. by 3 in. section takes five minutes this section may now be flame-cut in 1 minute 40 seconds, whilst with a 20 in. by 4 in. section the time is reduced from 25 minutes to 3 minutes by flame cutting. This tremendous increase in speed has, of course, decreased the man-power

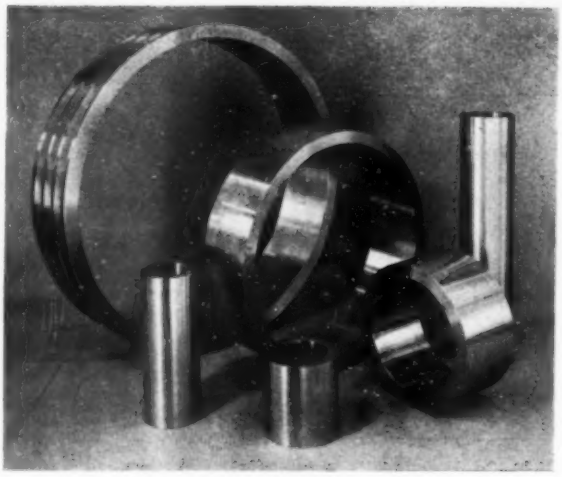


Fig. 4.—Centrispun castings in stainless steel.

TABLE I.—QUALITIES OF "STAYBRITE" STAINLESS STEEL

	F.S.T. STEEL	D.D.Q. STEEL	F.D.P. STEEL	E.M.S. STEEL
Typical Analysis	C 0·12 Si 0·60 Mn 0·80 Cr 18·0 Ni 8·5	C 0·10 Si 0·60 Mn 1·0 Cr 12·5 Ni 12·5	C 0·12 Si 0·60 Mn 0·80 Cr 18·0 Ni 8·5 Ti 0·60	C 0·12 Si 0·60 Mn 1·5 S 0·25 Cr 18·0 Ni 10·0 Mo 0·30 Ti 0·60
Relevant Specifications	BS: En. 58A DTD: 189	BS: En. 58D DTD: 189	BS: En. 58B DTD: 166B, 171B, 176A, 189, 571	BS: En. 58M
Physical Properties:				
Specific Gravity	7·94 (= 494 lb./cu. ft.)	8·01 (= 499 lb./cu. ft.)	7·90 (= 492 lb./cu. ft.)	
Modulus of Elasticity (tons/sq. in.)	Softened: 12,900 cold rolled: 11,000/12,900	Softened: 12,900	Softened: 13,000 Cold rolled: 11,000/13,000	
Thermal Conductivity, C.G.S. units	At 20° C. 0·036 At 100° C. 0·039	At 20° C. 0·037 At 100° C. 0·040	At 20° C. 0·038 At 800° C. 0·059	
Electrical Resistivity, Microhms/cm. cube	At 20° C. 72 At 100° C. 78	At 20° C. 70 At 100° C. 77	At 20° C. 73 At 800° C. 119·5	As for F.D.P. Steel
Coefficient of Thermal Expansion 20/100° C.	0·000017	0·000018	0·0000016	
20/300° C.	—	—	0·0000017	
20/500° C.	—	—	0·0000018	
20/700° C.	—	—	0·0000185	
Typical Mechanical Properties	Softened Cold Rolled Sheet (1) (2)	Soft-ned	Softened Cold Rolled	Softened
Yield Point, tons/sq. in.	18 52 69	15	18 26	15·8
Maximum Stress, tons/sq. in.	40 58 85	37·5	42 52	38·8
Elongation %	50 30 6	50	45 30	53
Reduction of Area %	50 — —	50	50 42	54
Izod Impact, ft./lb.	110 — —	—	80 —	50
Brinell Hardness	170 — —	160	180 225	175
Fatigue Limit, tons/sq. in. (10,000,000 reversals of stress unbroken)	17 — —	—	17·5 —	18·25
Heat Treatment Hot Working	Start 1150° C. Finish 900° C.	Start 1150° C. Finish 900° C.	Start 1150° C. Finish 900° C.	Start 1170° C. Finish 900° C.
Softening	Quick cool 1050° C.	Quick cool 950/1050° C.	Quick cool 1050° C.	Quick cool 1050° C.
Maximum Service Temperature	300° C.	300° C.	800° C.	800° C.
Welding Properties	Good, but only recommended for applications involving mildly corroding condition.	Good, but should only be used for the less onerous conditions of service.	Good, may be welded without subsequent heat-treatment.	Weldable without subsequent heat-treatment.
Pressing or Forging Properties: Cold	Good.	Very Good.	Good.	Fair.
Hot	Good, but subsequent heat-treatment necessary.	Good, but subsequent heat-treatment necessary.	Good.	Fair.

required for the same output, but as far as the running costs are concerned these have not, as yet, been reduced in the same proportion, since the cost of powder flux is the controlling factor and the method of introducing it is only 50–60% efficient. However, in spite of these difficulties, which are likely to be overcome in the near future, the method should prove less expensive than cold sawing.

Heat Resisting Steels

Progress in the field of special heat and creep-resisting steels for gas turbine applications has been made with the introduction of the new Firth-Vickers 326, 337, 448 and 467 steels. These steels are required to withstand high stresses at high temperatures and they have to give a long period of reliable service if a prime mover of this nature is to compete with present forms of motive power. The 326 and 337 qualities are high alloy austenitic steels which have been produced successfully as turbine blade stampings. From the former steel, large rotor forgings can be produce[1], while the latter steel is suitable for discs. The third steel in this new series is the 448 quality which is a ferritic steel and which has proved particularly suitable for aircraft turbine components, such as discs, where high proof properties are required and where the service temperatures are not so high as to warrant the use of an austenitic steel. Another recent development is the 467 quality, an austenitic steel which has very high creep-resisting properties although the analysis does not include the more scarce and expensive alloying elements upon which steels of this nature usually depend for their creep resistance.

Centrispun Castings

Further progress has been maintained in the production of rings for a variety of purposes (see Fig. 4) outside the original application for aircraft components, by the centrispinning process. This consists essentially of pouring liquid steel into a rapidly rotating mould in such a way that the metal is directed by the centrifugal force to take up the shape of the mould. Experience has proved that this process is reliable and relatively cheap for steels which by their special composition are more difficult to manipulate in wrought form.

Precision Castings

At the other end of the scale very small components are being made by the lost wax method of precision casting. Firth-Vickers have been developing this process with corrosion and heat-resisting steels for some time, and precision cast components are now available in a wide range of these steels. It is important to note, however, that it is generally only economical to use this method for the production of small items which if produced by other methods would involve costly machining and finishing work. Components which proved very difficult indeed to machine are now being cast to a high degree of accuracy.

In a short article such as this it is not possible to give an adequate account of the great amount of work and research that continues to be done, but in general this is all directed to the same end, namely, to meet the increasing demand for these products, to ensure an even better quality, and to produce new steels to meet the exacting service demands of designers and engineers.

SHOWING TYPICAL ANALYSES, PROPERTIES AND TREATMENTS.

F.S.L. STEEL	F.C.B. STEEL	F.M.L. STEEL	F.M.B. STEEL	254 STEEL
C Si Mn Cr 0·05 0·60 0·80 18·5 Ni 10·0	C Si Mn Cr 0·12 0·60 0·80 18·0 Ni Cb 10·0 1·2	C Si Mn Cr 0·07 0·50 0·80 18·0 Ni Mo 9·5 1·25	C Si Mn Cr 0·07 0·30 0·80 18·0 Ni Mo 8·5 2·75	C Si Mn Cr 0·07 0·40 0·80 18·0 Ni Ti Mo Cu 18·0 0·60 3·75 2·4
BS: En. 58E DTD: 189	BS: En. 58F DTD: 176A, 571, 171B	—	BS: En. 58J	—
7·93 (= 494 lb./cu. ft.) Softened: 13,000 Cold rolled: 11,000/13,000 At 20° C. 0·038 At 20° C. 70 0·000016 — —	7·93 (= 494 lb./cu. ft.) Softened: 13,100 — At 20° C. 0·038 At 700° C. 0·048 At 20° C. 72 0·000017 0·000018 0·000018 0·000019	7·93 (= 494 lb./cu. ft.) Softened: 13,200 — At 20° C. 0·040 At 100° C. 0·045 At 20° C. 76 At 100° C. 82 0·000017 — — —	7·96 (= 496 lb./cu. ft.) Softened: 13,200 — At 20° C. 0·039 At 100° C. 0·042 At 20° C. 78 At 100° C. 84 0·000 016 — — —	8·04 (= 501 lb./cu. ft.) Softened: 13,000 — At 20° C. 0·031 At 20° C. 85 0·000017 — — —
Softened 15 40 60 65 80 160 17	Softened 17·2 40·8 58 65 80 175 19·5	Softened 17 40 50 50 80 180 17·5	Softened 18 40 50 50 80 180 17·5	Softened 18 39 17 66 80 160 17
Start 1150° C. Finish 900° C. Quick cool 1050° C.	Start 1150° C. Finish 900° C. Quick cool 1050° C.	Start 1150° C. Finish 900° C. Quick cool 1050° C.	Start 1150° C. Finish 900° C. Quick cool 1050° C.	Start 1150° C. Finish 900° C. Quick cool 1050° C.
300° C.	800° C.	—	—	—
Good, post welding heat-treatment not necessary.	Very good, no heat-treatment after welding is necessary.	Good, heat-treatment after welding unnecessary.	Good, heat-treatment after welding unnecessary.	Good, may be welded without subsequent heat-treatment.
Very Good. Good.	Good Good.	Good. Good.	Fair. Fair.	Fair. Fair.

Solders and Soldering : Some Recent Advances

By H. C. Watkins, L.I.M.

Research Department—H. J. Enthoven & Sons, Ltd.

There has been steady progress, in recent years, in the development of solders, as well as of techniques designed to ensure their most effective application. Although it has been impossible to discuss all recent developments in this field, the present review indicates that significant advances are being made and it is noteworthy that further work is in progress from which important improvements are expected.

DURING the latter half of World War II, restrictions were imposed on the use of tin and tin-containing materials when the Allies were cut off from their main sources of supply of this metal in the Far East. Economy in the use of tin became a wartime necessity : to-day, the tendency to economise in the use of tin, and, therefore, in solder, arises from a different cause—the high price level. In view of the need to increase production rates in order to provide more goods for export and for the home market, measures introduced to effect solder economy must on no account lead to a decrease of efficiency in the factory, nor must the quality of the product suffer. Wartime experience showed that a reduction in the tin content of the solder used for a particular operation did not always ensure a saving of tin. In some factory trials it was found that owing to difficulties of application arising from the use of a solder of lower tin content, a greater quantity of solder was consumed and this outweighed the expected tin economy. At the same time, production rates fell. To-day, solder economy may be effected by the use of novel and improved soldering techniques. The achievement of maximum economy without loss of efficiency depends both on the ingenuity of the consumer and on the use of high quality solder products.

Wiping Solders

The importance of solder quality in controlling the speed of the soldering operation and the quantity of solder usefully employed is to be seen very clearly in car body filling operations. The solder, containing generally 25–30% tin, is applied from a stick or ladle to pre-tinned seam welds and other surface depressions requiring to be built up. Pre-tinning is carried out conveniently with the use of solder paint, a product which will be referred to again later. When a stick is used it is heated at one end with a gas/air torch until the solder just begins to run, the pasty metal at the end of the stick then being transferred to the pre-tinned and heated surface. With solder of the correct quality for this class of work, the pasty metal can be wiped smoothly from the still solid portion of the stick by pressure against the surface being built up. With unsuitable material, cracking will occur in the solder adjacent to the pasty metal as soon as pressure is applied to the stick. If this friability is at all marked, much of the solder will not adhere, especially when the surfaces to which it is being applied are inclined to any extent from the horizontal, with the result that the operation is unnecessarily difficult and prolonged—a matter of some concern on a car body assembly line.

This anomalous behaviour of solder with tin contents in the range indicated above has been found also by plumbers making wiped joints by the method involving application of solder from a stick : they often describe solder which exhibits this hot-friable character as "chalky." Extensive investigations into the cause of the friable nature of the unsatisfactory solder have so far not yielded a full fundamental explanation based either on chemical analysis or microstructure, but a procedure which ensures the production of suitable material has now been devised.

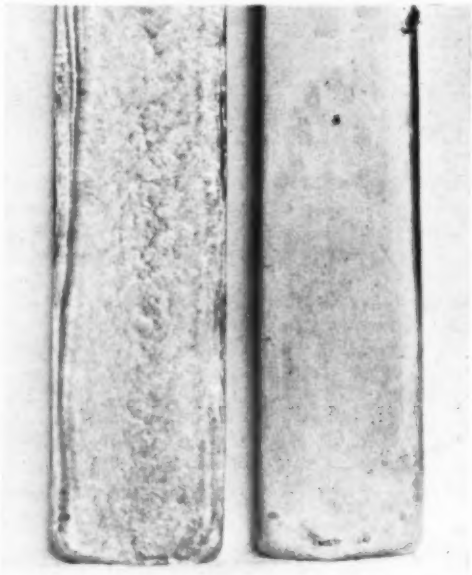
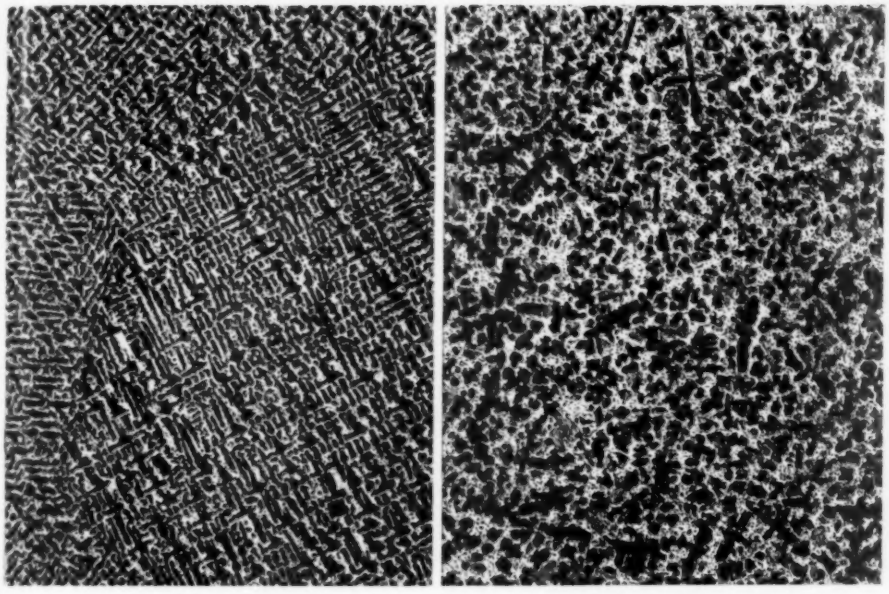


Fig. 1.—Cast surface of sticks of 28% Sn, 1.6% Sb solder before (left) and after (right) sulphur treatment.

Coarse-grain solder, sometimes referred to as "sandy" by plumbers, is generally regarded as being more liable to give unsound wiped joints than is a fine-grain material. A considerable degree of grain refining and a more uniform texture is obtainable by the addition to the solder of 0·1% arsenic.[1] The same addition is also said to reduce dross formation. Grain refinement is usually obtainable simply by stirring a little sulphur into molten solder. The surface appearance of a bar of naturally coarse-grain solder before and after treatment in this manner to refine the grain is shown in Fig. 1, and the corresponding microstructures in Fig. 2. It has been shown that naturally coarse-grain solder grain-refined

1 Schumacher, E. E. *J. Inst. Metals*, 1950, **78**, 1.



Before sulphur treatment. After sulphur treatment.

Fig. 2.—Microstructures of solder sticks shown in Fig. 1. ×100

in this way can be made to revert to a coarse grain by centrifuging to remove the crystallisation nuclei.

Even when a fine-grain wiping solder is assured, a porous joint may still result if the plumb is at all massive. The slow solidification of the solder may allow gravity draining of the liquid phase, resulting in the formation between the primary crystals of minute fissures which may be interconnecting and lead to gas unsoundness—an inadmissible fault when gas-filled telephone cables are being considered. According to a recent proposal for overcoming porosity,[2] a layer of low-melting lead-tin-bismuth eutectic (lead 32, tin 15·5, bismuth 52·5%, mp. 95° C.) is applied by rubbing a stick of the fusible alloy over the joint as soon as wiping is completed. The residual heat in the joint melts the fusible metal which is said readily to wet and penetrate into the capillary-like fissures in the solder, thus effecting a seal. Whilst this method appears to offer a reasonable solution to a longstanding difficulty, the high price of bismuth may limit its application.

Soldering Aluminium

With the development of aluminium sheathed cables special techniques have had to be evolved for their jointing by soft soldering. In one method, already in successful use in this country, a normal wiped joint is made between the aluminium sheath and a lead sleeve after pre-tinning the end of the sheath with 90/10 tin-zinc solder. The aluminium is filed clean, heated with a blow lamp and solder applied from a stick over the area to be tinned without the use of a flux. Tinning is completed by vigorous scratching of the aluminium through the layer of molten solder with a wire brush, any excess solder being afterwards wiped off. Aluminium stranded conductors and cable sheaths are also reported to have been soldered successfully in the United States with the aid of a special flux[3] which makes it possible to dispense with abrasion during tinning. Considerable interest is being displayed in industry in the application of supersonics to facilitate the soldering of aluminium and its alloys. A supersonic soldering iron,[4] designed for factory use, is now being manufactured in this country and a prototype of this instrument has been made available for testing in the laboratories of H. J. Enthoven & Sons, Ltd. It has been established by the designers of the iron that the action of supersonics in removing the oxide film on aluminium and so allowing tinning to take place is one of cavitation erosion.[5]

Owing to the danger of corrosion, soldered joints in aluminium are generally given a protective coating of, for example, bitumastic paint, with the object of excluding moisture and so preventing electrolytic corrosion and the rapid failure of the joints. Recent American work[6] has indicated that joints made with 95/5 zinc-aluminium eutectic solder, with or without 0·01% titanium, are as strong as joints made with the available commercial alloys when freshly prepared, but are more resistant to corrosion when exposed to weather in an industrial atmosphere, an air-water vapour atmosphere at 95° C., and salt spray. Included in these tests were two patented compositions, viz. tin 60, cadmium 20, zinc 15, copper 2·5, silver 2/5%; and tin 74, lead 20, zinc 6%, a conventional 70/30 tin-zinc solder, and the German material "Alu-Tinol" (zinc 43, tin 35, cadmium 14, lead 8%). The relatively high melting point of the zinc-aluminium eutectic (354° C.)* would however, no doubt exclude its use for the finer soldering operations.

Another point that must be borne in mind when soldering certain aluminium alloys is the possible embrittlement of the joint area as a result of intercrystalline penetration by solder during tinning with zinc-containing solder. A recent investigation[7] has shown that cold-worked fully heat-treated aluminium-magnesium-silicon alloy (HS. 10–WP) and fully heat-treated aluminium-magnesium-zinc alloy are particularly susceptible to this trouble, whilst pure aluminium and the aluminium-manganese alloy, NS.3, whether work-hardened or annealed, and the aluminium-magnesium alloys NS.4 and 5 when annealed, are free from any tendency to the defect.

Special forms of Solder

There is a growing tendency in industry to replace hand-soldering by automatic or semi-automatic methods,

2 Phipps, G. S. *Bell Labs. Rec.*, 1950, **28**, 295.
3 U.S. Patent 2,286,298.

* Inst. Metals Annotated Equal. Diag. No. 1 gives 382° C.
4 Anon. *Metallurgia*, 1949, **41**, (242), 104.
5 Noltingk, B. E., and Neppiras, E. A. *Nature*, 1950, **166**, 615.
6 Roberts, C. W. *Metallurgia*, 1950, **42** (249), 55.
7 Anon. *Metallurgia*. 1950, **42** (250), 131.

thereby reducing labour costs and solder consumption. Special solder shapes are required for these newer soldering procedures, the solder being applied for example in the form of a pellet, ring, washer, ribbon or foil, the quantity being just sufficient to ensure the production of a sound joint. An external flux is applied, unless the pre-formed solder is flux-cored, and the components then heated to the soldering temperature by any convenient means, which may include, for example, passage through an oven or over controlled gas flames, or the use of high frequency heating equipment.

Where there is a multiplicity of joints to be made in an assembly, as with heat exchangers, it is often found more convenient to apply the solder in powdered form mixed with flux and a suitable binder. These solder paints may be applied by brushing or spraying, or the assembly may be given a coating by immersion in the paint after thinning it to a suitable consistency. After application of the paint the work is heated in order to fuse the solder which is then drawn by capillary attraction into the joints. Although a solder paint containing a non-corrosive flux may be employed, by far the greater proportion contains an active zinc chloride based flux, the residue from which must be carefully removed by washing after soldering.

Flux-cored Solders

The evolution of the modern flux-cored solder wire is closely linked with the development of the electrical industries which created the need for more rapid and reliable methods of soldering. The advantage of the greater speed of soldering made possible by the use of cored solder, due to the application of flux and solder in one operation, needs no emphasis ; other advantages to be derived from making the flux an integral part of the solder wire, although possibly less obvious, are nevertheless of the greatest importance. Thus, the use of cored solder ensures that an appropriate quantity of flux is always applied, and that the solder is ready to flow when the flux is in its most active condition. It also provides an additional factor of safety when a non-corrosive flux is specified, there being no possibility of accidental contamination during use in the factory as may occur when an external flux is employed.

Present day cored solders bear little resemblance to the first crude forms which appeared towards the end of the last century and it is true to say that they are almost entirely free from the defects associated with these early flux-filled solder wires. In particular, the danger of voids in the flux core can now be eliminated as a result of improvements in the manufacturing process.

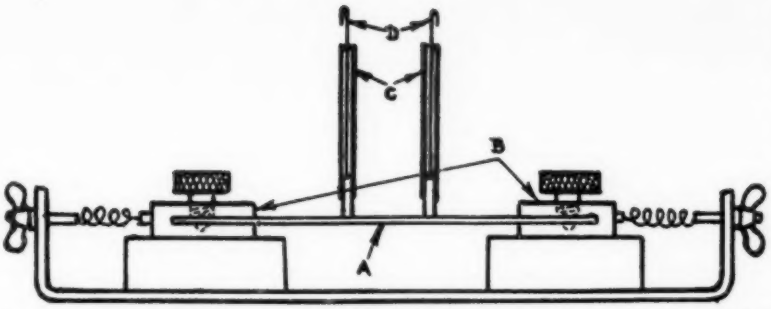
Variations in the shape of the core and its disposition within the solder wire have been proposed from time to time whereby the performance of the cored solder is claimed to be improved in comparison with material having a circular core at the centre of the solder wire. These claims are difficult to substantiate adequately by means of laboratory tests and, consequently, an evaluation of their true merit can be arrived at only as a result of carefully supervised factory trials in which records are made of soldering speed and solder consumption. Whatever the core shape or distribution employed, the ratio of flux to solder must be carefully controlled during manufacture in order to ensure the presence of just the correct quantity of flux for efficient soldering. For general purposes a flux core 2% by weight of the total is usually found satisfactory.

Rosin or colophony, consisting primarily of abietic acid, is still the most widely used material as a flux for cored solder, largely because the residue remaining after soldering fulfils two essential requirements of the electrical industries—it is non-corrosive and has a high insulation resistance. Being a natural product, rosin can vary appreciably in composition and degree of purity and considerable research has been devoted to the study of the suitability of the various grades as soft soldering fluxes. An important criterion in the choice of a supply of rosin is that the quality of successive deliveries shall be as constant as possible. Generally speaking, the lighter grades are to be preferred, not only because these approach more nearly the ideal material of constant chemical and physical properties but because they have the psychological advantage of leaving a "cleaner" residue.

Although plain rosin-cored solder is still produced in considerable quantities it is found to be too slow acting for many soldering operations since rosin possesses only a limited power to dissolve or disperse those oxide or other films which hinder or even prevent wetting of a metallic surface by solder. When a manufacturer is soldering such large numbers of joints that high production rates must be maintained if production is to be economical, as for example, in the assembly of many electronic units, there is a real danger that the use of a plain rosin flux may lead to some joints being imperfectly soldered. At the worst, there may be a blob of solder on the joint which is, however, actually insulated from it by a layer of rosin : here one has a "dry" joint and if this condition does not become evident at some stage of inspection the equipment is almost certain to develop faults in service owing to the variable and probably high resistance of the unsoldered connection. It is sometimes possible to rectify such imperfectly soldered joints simply by re-heating, but such a procedure, besides increasing the soldering time, may cause damage to heat-sensitive components adjacent to the joints.

An important step forward was taken when an attempt was made, about twenty years ago, to increase the effectiveness of rosin as a fluxing medium by incorporating in it a small percentage of a highly active fluxing agent with the object of producing a fast working flux coupled with the desirable qualities of the rosin residue. To-day, a very large proportion of the solder employed in the radio and associated industries has an "activated" flux core. This development is now so marked that the British Standard 441 for cored solders is at present being revised to embrace activated as well as plain rosin cores.

The development of the modern activated rosin cores has involved much painstaking research on the part of the manufacturers and it is not surprising, therefore, that the majority of the compositions now in use are either protected by patents or have not been disclosed. Before a new activator is adopted it must be ascertained, as the result of careful laboratory tests carried out under a variety of conditions of temperature and humidity, that the rosin residue is free from corrosive effect on the materials being soldered and that any fumes evolved during soldering are harmless if deposited on adjacent components. Such tests have shown that even with components wound with extremely fine gauge copper wire, soldering with the use of a suitably activated rosin flux may be carried out without any detrimental effect. Unfortunately, some of the activated rosins first



A—Test strip ; B—Spring tension clamps ; C—Guide tubes for solder wire ; D—Weights

Fig. 3.—Diagram of principal features of solder performance tester.

produced were not subjected to the rigorous tests now imposed with the result that a certain amount of understandable, but now unjustified, prejudice has arisen in some sections of the electrical industry against the use of activated cores owing to the deleterious effects of these early materials.

Solders used in the production of rosin-cored wire are lead-tin binary alloys. The compositions most favoured for general electrical work are 60/40 and 45/55 tin-lead, whilst 20/80 tin-lead is employed for the soldering of the filament connecting wires to the sole plates of electric lamps.

Although the greater proportion of cored solder is consumed by the electrical industries an increasing tonnage is being used for soldering operations where previously blowpipe or solid wire solder was employed in conjunction with an external flux. For many of these uses a rosin residue on the soldered parts is undesirable, especially if the parts have afterwards to be cleaned prior to a finishing operation such as electroplating. Here a water soluble flux residue is to be preferred and cored solders containing suitable fluxes are available. These fluxes are highly active and are effective in the soldering of many metals, such as steel, with which the ordinary rosin-based cored solders do not perform satisfactorily.

A simple technique for testing the performance of cored solders has been described[8] in which the effectiveness of a particular solder/flux combination is evaluated on the basis of the extent of wetting and spreading occurring during a short time interval, generally not exceeding five seconds, on a particular metal in a given condition. Rates of heating of the same order as those obtaining in actual soldering operations are achieved by passing a heavy current at low voltage through a strip of the metal which is clamped at each end to a copper block ; the strip is held taut throughout the test by means of tensioning springs (see Fig. 3). The cored solders are applied in the form of standard short lengths cut off square and supported vertically in small-bore glass guide tubes so that both solder and flux are in contact with the strip. Control of the rate of heating is by means of a variable auto-transformer in the primary circuit of the transformer, the duration of the heating cycle being controlled through the operation of an automatic timer. The general arrangement of the apparatus is shown in Fig. 4. A clear differentiation between a plain and an activated flux core may be obtained by tilting the specimen (of nickel, for example) at an angle of about 30° to the horizontal. In these circumstances solders having plain rosin cores do not adhere but run off as soon as they melt, whereas those with activated cores wet and spread on the specimen. The extent of spreading obtained on a horizontal surface in a short time interval may be used as a criterion of the effectiveness of differently activated flux cores. Spreading tests may be made on any material to be investigated so long as it is available as sheet or strip approximately 0·005 inch thick.

It will be clear that the usefulness of the apparatus is not confined to the evaluation of cored solders ; it may also be employed to determine the effectiveness of liquid or paste fluxes when used with particular solder compositions.

Physical Considerations

It is appropriate at this point to refer to the importance of surface condition, particularly roughness, as influencing the spreading of solder over a solid metal surface. It has been shown[9] that the contact angle which a liquid makes against a rough solid surface depends on the form as well as on the degree of roughening. When the surface consists of intersecting capillary grooves and the specific contact angle θ of the liquid against the solid (determined by the balance of the surface tensions at the three surfaces solid-liquid, liquid-gas and solid-gas) is less than 90°, the contact angle tends at once to θ then more slowly to a smaller value ϕ. ϕ is related to θ by Wenzel's expression, $\cos\phi = r\cos\theta$ where r = "roughness ratio," i.e. actual surface area/nominal surface area. When the roughening takes the form of isolated pits, on the other hand, the observed contact angles are greater or less than the true (specific) angle according as the liquid reaches a position of metastable equilibrium by advancing or receding over

[8] Bailey, G. L. J., and Watkins, H. C. *Metal Ind.*, 1949, **75**, 551.

[9] Shuttleworth, R., and Bailey, G. L. J. *Discussions Faraday Soc.*, 1948, No. 3, 16.

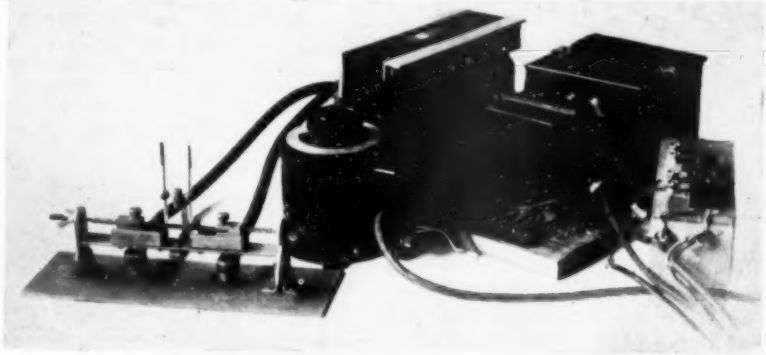


Fig. 4.—General view of apparatus for testing performance of solders.

the solid, i.e. the contact angle exhibits hysteresis. The inference to be drawn from these considerations from the point of view of practical soldering is that surfaces prepared for soldering by mechanical means, such as abrading with emery paper or scratch-brushing, are likely to be more receptive to solder than pickled surfaces, since the former approximate to ideal grooved surfaces whilst the latter are often pitted, and thus less wetting may occur.

Another factor which may affect the spreading of a liquid metal over an otherwise clean solid metal is the incidence of adsorption upon it of atoms of the liquid metal. A recent investigation[10] of surface tensions in the system solid copper-molten lead showed that the surface tension of copper exposed to an argon or hydrogen atmosphere containing lead vapour at a partial pressure of the order of 0·1 mm. Hg, has a value of rather less than half that found in the absence of lead. It is suggested that the reduction in surface tension is due to adsorption of a mono-layer of lead at the copper-gas surface and that this finding offers an explanation for the failure of lead to exhibit a contact angle of zero against solid copper surfaces, as would otherwise be expected from a consideration of previously available surface tension data.

Whilst it has been impossible to touch upon every recent development of interest in the solder field within the compass of this brief review, it will be evident from the foregoing that significant advances are being made in many directions. Further work is in progress in our own and other laboratories known to the author and important improvements both in the quality of solder products and in methods of their application may be expected in the not too distant future.

10 Bailey, G. L. J., and Watkins, H. C. *Proc. Phys. Soc., B*, 1950, **63**, 350.

Plastics for Protective Coatings and Linings of Chemical Plant

By E. E. Halls

Various useful processes have long been available for providing protection to mild steel under service conditions. During recent years, however, a variety of grades of plastic materials have been developed for specific needs and have been applied for this purpose. Although considerable care is necessary in making a selection, because each has its limitations, their use has solved many problems. Various methods are employed to provide the protective coatings and both the methods and the plastic materials are discussed.

MILD steel is probably the most economic and most easily manipulable material for plant construction, and autogenous welding of this material has become established as a sound method of fabrication. Various useful processes have long been available for providing protection under the conditions of of service; these include vitreous enamelling, metal spraying, stove-enamelling, etc. Non-corrodible metals and alloys have been developed in the sense that they provide resistance to specific conditions of service. These include aluminium, copper, aluminium bronze, stainless steel, Monel metal and silver. Nevertheless, the needs of engineering, chemical engineering and metallurgical industries are by no means satisfied from the numerous possibilities in these directions. Not only do factors of cost and amenability to fabrication into specific shapes limit the selection of materials, and the problems associated with fittings such as valves and cocks, pumps and pipe lines, and exhaust systems, but very often a material that gives good service under a closely defined set of conditions, fails if processing factors such as temperature, concentration, impurities and the like deviate far from the optimum values.

Attention has been given to the possibility of employing the synthetic plastic materials with the object of reducing initial plant cost, prolonging plant life and decreasing maintenance effort. During the last thirty years, not only has a number of basic plastic materials become available, but a variety of grades of each has been developed to suit specific needs. The application of these to plant in which corrosive conditions obtain, has solved many problems. At the same time, selection must be very discerning because the plastics, although many of them offer considerable inertness to chemical attack, also have their limitations. Methods of fabrication are restricted; generally there is a strict upper temperature limit for safe operation; some of them are not very resistant to alkalies, nor to strongly oxidising solutions; stress and strain may lead to complications and photo-ageing cannot always be ignored. At the same time, with sound selection of material, excellent service is possible from a plastic material for plant construction or as a protective coating or liner. It is this use as a covering that offers greatest possibilities, because it enables the cheapest material and form of construction, e.g., welded mild steel, to be extensively adopted.

The plastics for the purpose in question include rubbers, chlorinated rubber, polyvinyl resins, polythene and phenolic resins, and, in providing coatings, they may be applied by hot spray, or from solution by dip or spray, or by fitting in sheet form and cementing or welding. Some of them may also be applied as a dough or paste and cured in position, or as powder to the hot articles with subsequent flowing by thermal treatment. Each method has its merits and demerits, and these will be discussed below.

Hot Plastic Spray

Thermoplastics and thermosetting resins in the form of graded powder can be applied through a flame gun in much the same way that metals are powder-sprayed. The metal to be so treated must be chemically clean.

that is, free from oil and grease which would impair adhesion, and free from corrosion products such as rust and loose scale. It is advantageous although not essential for the surface to be roughened, for example by abrasive blasting. In the spraying operation, a flame is maintained at the nozzle of the gun by feeding it with oxygen and a combustible gas such as hydrogen or propane ("Propagas"). The plastic powder is picked up on the injection-principle in a by-pass from the main compressed air steam, which in turn carries it through the nozzle and flame of the gun, and propels the softened particles on to the work surface. The latter may be preheated by the flame of the gun. The plastic particles flatten upon impact with the work surface, and become saucer-like in shape. The coating is thus built-up of interlocking particles, and its porosity can be reduced by travelling the flame over the coating at intermediate stages of the spraying operation, thereby superficially flowing the plastic and sealing its surface.

The adhesion of the sprayed plastic film is determined by the nature of the plastic itself, the nature of the metal base, degree of surface roughness, differential contraction of plastic coating and base material, and on the temperature of the sprayed material. The spraying temperature needs to be judiciously chosen because, although the plastic needs to be as close to its melting point as possible in order to impart maximum plasticity and to promote adhesion, yet it must be as low as practicable to minimise oxidation. Hence, a nice balance of conditions has to be arranged.

The flame gun referred to is designed, and many processes for plastics patented, by Schori Metal Processes Ltd. Materials applied in this way include shellac, a mixture of shellac and powdered glass, bitumens, synthetic rubbers, phenolic resins, the so-called synthetic rubber "thiokol" and polythene. The base metal coated may be of any composition, and has included aluminium and magnesium alloys as well as steel.

The asphalts or bitumens flame-sprayed in this manner, are chosen to yield tough, adherent coatings which, apart from being highly impermeable to moisture vapour and corrosion resistant, will withstand hard wear and impact shock. This type of coating is a possibility for exhaust ducting, and structural work in general, and for the exterior of pipe work and exterior surfaces of tanks, etc. The use of the flame gun is not limited to metal work, and wood, brick and concrete may also be coated, so that the bitumen coatings may be applied to walls and floors.

Synthetic rubbers have been sprayed on metal work, including containers and duct work for plant for metal finishing processes, i.e., electroplating, anodising and chemical colouring, and for acid treatments and chemical processing in general. A natural rubber-sulphur mix can also be sprayed for similar applications, choosing the sulphur content to vary the final product from soft and flexible to hard and ebonite-like. Thiokol has been specially used for resistance to hot combustion gases, as well as in applications for chemical and general corrosion resistance.

A flame-sprayed thiokol coating on one side of a $\frac{1}{8}$ in. thick mild steel sheet was subjected to salt spray for six months. The test used 20% salt solution atomised by compressed air at room temperature during the eight hour day, leaving the specimen in the mist laden cabinet overnight. It was then washed in water, dried on a cloth and examined. At the end of six months, rusting from the bare steel edges had progressed beneath the thiokol coating to an extent of not more than $\frac{1}{4}$ in. Beyond that, there was no evidence of attack on the steel beneath the thiokol film, and the latter showed no signs of deterioration. It withstood scratch tests for adhesion without flaking or chippiness both before and after the test, and retained its hardness. This type of coating withstands impact shock quite well, although it is not flexible, e.g., on bending the $\frac{1}{8}$ in. sheet around a radius equal to its thickness, the coating cracks and flakes from the crack.

A similar specimen coated on one side only with thiokol was immersed in 10% hydrochloric acid for 4 hours; the properties of the coating were unimpaired and there was no evidence of any penetration of acid between the coating and the steel.

Coatings of shellac and asbestos, and shellac and mica or powdered glass, have been used for resistance to specific conditions of heat and chemical corrosives. These mixtures yield hard, non-flexible coatings. Tested on aluminium alloy castings, prepared by shot blasting, black shellac compound coatings of thickness of the order of 0·010 in. showed excellent adhesion on scratching, but being hard and non-flexible, they naturally cracked and flaked slightly on bending. Under compression tests, detachment of the coating was confined to the lines of cracking of the casting. Under hot humidity conditions, the only change under the following test conditions was a change in colour to more grey :—

(*a*) 24 hours at 70° C., followed by two cycles each comprising 8 hours at 60° C. and 100% humidity, followed by cooling off with condensation.

(*b*) 30 cycles comprising 8 hours at 55/60° C. and 75% humidity, followed by cooling off to room temperature with rise in humidity to 100% and condensation.

Polythene is one of the most suited thermoplastic powders for application by flame-gun. It is also most attractive because of its exceptional moisture proofing qualities, inertness, good resistance to acids and alkalies and to many solvents. When sprayed to form a complete envelope, adherence to the surface to which applied is exceedingly good because of its higher coefficient of contraction. One peculiarity of polythene is degradation of mechanical properties if subjected to oxidation conditions at its melting point. Consequently some deterioration of the material occurs during the spraying process, and the applied film does not possess the same homogeneity and mechanical strength exhibited by extruded sheet polythene.

The sprayed polythene coatings have been used for resistance to water and moisture penetration, and in particular for linings and coverings for chemical processing equipment. They have been used for electroplating equipment, including the coating of the cathode racks and jigs. These pass through hot aqueous alkali cleaners and acid pickles as well as through the electrolyte, and must withstand repeated cycles of these conditions as well as the wear and tear of handling.

It must, of course, be assured that the coating is uniform and free from weak spots, because a single point of weakness can lead to failure. For very strong oxidising agents, such as the concentrated nitric acid-fluoric acid mixtures used in the pretreatment of aluminium castings for electroplating, sprayed coatings are not entirely satisfactory. Oxidation appears to occur between the grains of the coating, so that after about seven days contact with such a solution, the polythene coating shows

evidence of flaking and de-laminating, and after 21 days' contact a film of 0·015–0·031 in. thickness may become penetrated, with attack on the base metal.

Polythene coatings are rubbery in nature and withstand impact shocks and do not chip or flake under scratch tests. Applied to shot-blasted aluminium castings, to a thickness from $\frac{1}{16}$–$\frac{1}{32}$ in., the finish became detached on bending or when subjected to compression tests. It withstood the hot humidity tests cited above under shellac coatings satisfactorily.

Polythene spray coated jigs can safely be passed through hot processing solutions short of boiling point, but for tank linings, processing temperatures should be limited to 60°–80° C.

Polythene Powder Coatings

Rather superior performance to that given by flame-sprayed polythene, is obtained by a cold powder application of this material to a hot object. In this procedure, the article, e.g., jig, fixture, etc., is heated to a temperature above the melting point of polythene (110°–120° C.), and is then immersed in a tray or container of polythene granules, and agitated till it cools. The polythene adheres to the article, giving a more or less uniform covering, which is granular in appearance, fully fused at the surface of the object, and unfused on the outer surface. Fusion is completed by an oven heat treatment, to yield a smooth impervious coating. To aid coverage and adhesion the object must be clean, it can usefully have been roughened by abrasive blasting, and, in its design, sharp edges and corners, re-entrant angles, blind holes and the like should be avoided.

The polythene employed should contain the usual anti-oxidant or thermal stabiliser. The coating shrinks tightly on to the base metal but does not adhere except by virtue of providing an envelope. The coating is inert to chemicals, and aqueous solutions, and suffers no dimensional changes under wet and dry conditions within the limitations of its melting point.

Solutions for Dip and Spray

The development of solutions for immersion treatment of the article to be coated has been mainly directed towards application to jigs, racks and suspenders employed in the electroplating industry, where it is desired to provide an insulating covering for the avoidance of electrodeposition on any surfaces other than those of the work itself. The article in these circumstances is usually of copper or brass, and the plastic coating must withstand repeated cycles of operation, not only through the electroplating solution but also through preparatory alkaline and acid cleaning processes. It would also be useful to include solvent degreasing, i.e., trichlorethylene vapour or liquor-vapour in the process schedule, but to date a plastic coating for plating racks has not yet been commercially established for this added rigour, although one has just become available for which resistance to trichlorethylene is claimed. For application, the metal jig is preferably abrasive blasted and is then given a coating of special primer, which gives very good adhesion to the dipped plastic coating. The latter is of a soft, resilient nature.

Apart from chemical and temperature considerations, tenacity and mechanical strength of the covering must be considered. Such jigs and fixtures suffer very heavy wear and tear, especially in manually operated plants, and it is essential that the coating should withstand the impact shock of knocking against the edge of tanks and of relatively rough handling. To assist this, attention must be given to the design of the articles to be covered. Sharp edges and corners can be avoided; inserts such as pins, spring wires and clips, can be firmly anchored so that they do not tend to turn or otherwise move and so rupture the coating.

In the electroplating jigs, the main hook of the suspension must be bare to make metallic conducting contact with the bus-bar and the actual supports for the work must likewise be free from coating. Generally, the coating is removed from these portions after dipping and curing or drying. This raises another important point, namely, the coating must either present excellent true adhesion to the metal, or it must shrink tightly on to it, otherwise the various processing solutions through which the jig passes in fulfilling its normal function, will seep between the covering and the metal jig. This failing would cause trouble, either from possible corrosion of the metal beneath the coating, or from gradual contamination of process solutions with carry-over from previous solutions. In fact, both faults may be encountered.

The attractiveness of solutions for dip treatment is accounted for by low cost, and simplicity of use; in some cases repairs can be easily effected. These represent major advantages over vulcanized rubber-coverings. The use of dip solutions need not be confined to chemical finishing processes of plating, anodising, metal colouring and chemical metal pretreatment in general, but can be extended to chemical processing as a whole. Thus uses can be profitably found for this type of protection for, stirrers, or stirrer-blades, thermometer sheaths, ladles, measuring devices, small containers, etc. Naturally the nature of the covering must be given consideration in relation to the particular chemical or mixture of chemicals concerned.

One of the first materials of this category to give satisfactory service was a rubber-hydrochloride base plastic marketed under the proprietary name of Korolac. It is supplied as a gel, which liquefies on heating. The work to be treated is thoroughly cleaned and immersed in the solution at 85°–93° C. A double lined tank is preferred for the purpose, with the plastic indirectly heated with electric immersion heaters in oil in the interspace. Exhaust can be provided to remove solvent fume when the dipping is in progress, but a cover is provided for the tank to avoid undue loss of solvent when it is not in use. The inner tank needs to be vitreous enamel lined.

The clean, cold jig is dipped and steadily withdrawn and allowed to drain back into the tank. Any "strings" of plastic that form are immediately pulled off, which allows the coating to re-seal at these points. The coating is allowed to air dry overnight or in an oven at 45° C. for half-an-hour. Subsequent coats may then be applied to build up the requisite thickness. In all dippings, however, it is necessary to dip cold and withdraw immediately, as otherwise the base metal becomes hot and too thin a coat is secured.

The rubber hydrochloride type of coating has proved successful in ordinary electroplating processes entailing acids and alkalies not excessively strong and not too hot. Failure ultimately is from mechanical damage and peeling, because the coating only adheres by virtue of shrinkage as the solvent dries out to leave a continuous envelope. For example, to represent one automatic nickel plating process, test pieces with the coating simulating jigs were subject for 30 weeks to repetitions of the following daily cycles:—

1st day. Immersion at 70°/80° C. in an aqueous solution of 4 oz. of sodium carbonate and 4 oz. of sodium metasilicate per gal.

2nd day. Immersion in cold water.

3rd day. Immersion at room temperature in an aqueous solution of 8 oz. of sodium phosphate and 1 oz. of sodium cyanide per gal.

4th day. Immersion in cold water.

5th day. Immersion in 10% sulphuric acid (V/V) at room temperature.

6th day. Immersion in cold water.

7th day. Immersion in nickel plating electrolyte at 40°/45° C.

8th day. Immersion in cold water.

9th day. Allowed to dry in air.

The plastic coating exhibited no signs of deterioration.

In another study of this rubber-hydrochloride base coating, coated brass test jigs were passed through daily cycles of nickel electrolyte at 40° C., cold water, immersion in 64 OP industrial methylated spirit at room temperature, and air drying, the sequence being repeated for the 6 months' period. Again no deterioration occurred. In contrast with this, cotton taping followed by three coats of bakelite varnish, or three coats of this varnish direct, failed due to softening of the varnish in the spirit within two cycles, and special chlorinated rubber paint coatings had blistered and lost adhesion in 6 weeks.

Plasticised polyvinyl chloride is another coating applied from a liquid medium. The latter comprises a dispersion of P.V.C. in suitable plasticiser or mixture of plasticisers, giving a thick creamy liquid. The article to be coated is pre-heated and dipped in the cold liquid. It is withdrawn and allowed to drain and then stoved for a short period at a temperature of the order of 150° C. A tough rubbery coating having all the normal properties of flexible P.V.C. is obtained. It has no true adhesion to the base metal but if it forms a complete envelope, it shrinks tightly to the object by virtue of its mode of formation. Electrical properties are good, and resistance to chemical solutions is of high order, exceptions being strong alkalies and strong acids. Solvents leach out plasticiser, so that the coatings are unsuitable for use with them, except possibly for very occasional and brief periods.

Depending upon the nature of the plasticiser, these P.V.C. coatings are affected by aqueous solutions which does limit their life but not beyond the margin of economical service. Water is absorbed and gradually displaces plasticiser, presumably by a process akin to osmosis. Generally this results at first in an increase in weight and finally a reduction. Some corresponding fluctuations in dimensions may occur. The following test results indicate the trend of these changes in the plasticised plastic material :—

(*a*) Under dry heat at 60° C. negligible change in dimensions or weight in 3 days.

(*b*) Under moist heat conditions at 60° C. 2·5–3·0% increase in volume and 0·7–0·8% increase in weight in 7 days, with no further change in 30 days.

(*c*) Under complete water immersion at room temperature, the percentage increases are as under :—

	Volume	Weight
1 day	Negligible	0·8 to 1·0
7 days	2·5 to 3·0	2·5 to 3·0
30 days	5·5 to 6·0	4·5 to 5·5

Mild heat is thus shown to be not deleterious, but in passing this type of coating through successive aqueous processes, and at intervals allowing to dry-out, the swelling that results from immersion will tend to be reversed during drying, especially if at elevated temperature, and wrinkling, with finally rupture, will occur. In many instances, the comparatively low cost of stripping the coating and recovering, and the simplicity of doing this, is preferable and more economic than using, for example, a vulcanised hard rubber covering. However, another feature associated with this phenomenon must not be overlooked, namely, the possibility of the water absorbed by the P.V.C. covering replacing plasticiser, which is forced out into the aqueous solution. This may be objectionable to the process or to the products produced in the process. For example, interference with strongly oxidising solutions can be foreseen, and such an effect can be noted when plasticised P.V.C. coatings are employed, with chromic acid or dichromate solutions for anodising aluminium, chromium plating or chromate pickling and passivating processes. For their safe use in these cases, it has to be ensured that the total area of P.V.C. and the time for which it is in contact with the solutions, are such that any deterioration of the solution is more than offset by "drag-out" losses and their make-up with fresh chemicals.

Solutions based on vinyl resins such as polyvinyl butyral have been designed for the spraying of heavy envelopes over completed equipments to give protection against humidity, out-door weather and tropical conditions. Similar solutions are available for the coating of metal surfaces by dip or spray, or roller, to give temporary protection against mechanical damage, such as scratching, during storage, machine shop operations and assembly. Modifications of these solutions are available for providing protection to metal work against corrosive gases, fume, spray and solution. These plastic solutions are also designed to possess, within limits, a range of "strippability." Thus, to protect the inside surfaces of paint spray booths, an easily peelable material is employed, so that it can be removed by stripping, say once a week. On the contrary, to give corrosion resistance against acid smokes, a more permanently adherent plastic is chosen.

Colourless media of this kind can be used over stoved enamelled or cellulose finished metal work and these afford a means of protecting control gear and instrument panels, still retaining the attractive appearance of the equipment. When damaged, the coating can be peeled off and a new one applied.

In a similar category, is the hot-melt type of plastic, generally used to give protection from mechanical damage, chemical corrosion or weather or tropical deterioration, in both shipment or storage. The plastic base may be cellulose-acetate-butyrate or ethyl cellulose, heavily plasticised. Both are employed in America, but the material usually utilised in this country is ethyl cellulose heavily plasticised with mineral oil. The compound is melted in an indirectly heated and thermostatically controlled stainless steel tank, and maintained at 180°–200° C. A hood is provided for exhausting gently when in use, and a cover for idle periods. The clean cold work is coated by dipping, and the thickness of coating is dependent upon the time of immersion and the temperature to which the article is raised in this time. For an average in-and-out immersion, the thickness of plastic covering acquired is from $\frac{1}{16}$ in.–$\frac{3}{32}$ in. A single

complete immersion may be employed, or one dip immersing about three-fifths of the work, followed by a second similar one with the article reversed so that the two coatings overlap. A flexible shrunk-on coating is the result, and at the end of its service period, it can be cut with a sharp wooden " knife " and peeled off.

This plastic dip process is ideal for small metal tools for storage, or for those which are used intermittently and that may corrode while lying in the factory. The peeled coating can be re-used, so that the only expense is that of coating ; the process can be operated on a small scale and so is attractive even for small chemical shops and for gauges in electroplating rooms.

A modified form of this plastic in solvent solution can be employed at room temperature, simplifying the plant entailed. It may be dipped or sprayed, and give a film thickness of the order of 0·005 in.

Linings from Sheet

Plastic coatings applied from liquids and paste by spray or dip are satisfactory and acceptable when expediency dictates, or when periodic stripping and replacement can be tolerated, and there are very many circumstances which fulfil these conditions. For more permanent installations and long service performance, liners from sheet material, which may range from 0·040 in.–¼ in. or even greater in thickness, are advisable. Such linings must be homogeneous and continuous, to which end they must be either welded or cemented with a medium appropriate to the plastic concerned. Polythene and rigid P.V.C. are the outstanding materials in this category, although others may be employed for special purposes. The lining may be fabricated in situ, or it may be prepared as a separate loose-fitting container which is then slid into position.

Polythene is employed on account of its inert nature, and chemical resistance even to strongly oxidising acids such as concentrated nitric, and to hydrofluoric acid. It melts at 110°–120° C., and so has a temperature limitation, and 60° C. is usually regarded as a maximum for continuous operation, although higher temperatures are safe for more intermittent working. For organic solvents many of which may safely be used in contact with polythene, temperatures above 60° C. should not be employed.

Polythene sheet ⅛ in. or ¼ in. thickness is usual for tank liners. This material may be bent or curved by heating to about 105° C. and shaping around suitable formers, and then rapidly cooled by quenching. It is joined by butt welding, using a hot-gas torch. The gas should be nitrogen, which is non-oxidising. The edges of the material at the butt-junction are bevelled to give a V-joint, and the weld is completed using a " filler-rod " of polythene.

" Rigid P.V.C." is polyvinyl chloride containing the usual stabilisers and lubricants but free from plasticiser, so that unlike the P.V.C. paste coatings, it is free from the ingredient that may sweat out or become displaced by water. It is consequently relatively very stable under hot and wet conditions. It can be bent and formed hot, and welded with a hot-gas (usually air) torch in a similar manner, except for a slightly higher temperature than that employed for polythene sheet. Again this material may be cemented into position as a lining, the junctions being reinforced by means of strips or angle pieces of the same material, also cemented. The cement employed is a special one developed for the purpose and the junctions are claimed to be almost equal to the parent material for strength, corrosion resistance and wear and tear. This adhesive method of construction is applicable to both metal and concrete.

The rigid P.V.C. has very good resistance to chemicals, almost equal to that of polythene. The temperature limitation, however, is of similar order.

Methyl methacrylate (trade name " Perspex ") in the form of sheet is another thermoplastic material that can be used as tank lining. It is joined to itself by means of a special dough-like cement, which dries out and polymerises to give virtually a homogeneous material which is essentially Perspex. The material is not normally welded, but as far as bending is concerned, it is similar to the other materials. It is not quite so chemically resistant, has the same temperature limitations, and is dimensionally stable.

In Perspex and in rigid P.V.C. shapes can be made from sheets at a controlled heat by a combination of vacuum and pressure or mould-shaping. For example a circular blank, heated and placed in a quick-clamp fixture to hold it around the periphery, can be drawn down by vacuum to the desired shape and extent, with an allowance for shrinkage on cooling. Alternatively, it may be drawn down by vacuum and then pressed back, by releasing the vacuum, so that it takes the shape of a former located in the cavity.

The three plastic sheet materials mentioned are relatively very stable in dimensions. Changes in volume and weight for polythene and for methyl methacrylate are nil or negligible over a test period of 12 months under conditions of dry heat at 60° C., wet heat at 60° C., or complete water immersion at room temperature. Rigid P.V.C. varies a little with source of manufacture and colour, but weight loss at 60° C. is negligible, and contraction in volume about 1·5% after 1 month or after 12 months. With wet heat at 60° C., weight change is again negligible, and volume increases at first up to about 1·5%, changing to a contraction after 6 months, losing about 3% in 12 months. In the case of water immersion, gradual absorbtion up to 0·25% occurs in a few weeks, with no further change in weight ; dimensions increase only in thickness, giving about 1·5% volume expansion in a few weeks, and then contraction, which reaches about 3% in 6 months, then remaining constant.

Details of chemical resistance of these materials are available from the suppliers. Polythene can safely be employed for long service with concentrated nitric acid or hydrofluoric acid ; rigid P.V.C. is rather less resistant. Both resist strong caustic soda. These facts give some idea of the extremely good performance of these materials ; they may also be employed in contact with many organic solvents.

Vulcanised Rubber

Reference must be made to hard and soft rubbers, hot vulcanised with sulphur, because they also fall in the category of plastics, and have for long been the main materials for chemical resisting linings. Generally speaking, rubber cannot be used with organic solvents, nor with fairly strong nitric acid and many oxidising agents. They are suitable for fluoric acid, and are extensively used for all the electrolytes and processing solutions (except strong sulphuric and nitric acids and their mixtures) employed in the electroplating industry. Hard rubber linings can be used up to 85° C. and special

synthetic mixtures such as ebonite formed from vulcanised Buna S are claimed to be satisfactory as high as 150° C.

Rubber liners are usually applied from dough to the article and vulcanised in situ. The hard "ebonite" types are most extensively employed. For large tanks that are built in sections, each section can be hard rubber lined, the coating being extended over the flanges. Assembly can then be by bolting with a soft rubber gasket to complete the chemical-resisting seal.

Some ingredients may be leached out of the hard rubber into the chemical solutions employed therewith, and they may be detrimental. In the case of phosphatising solutions operated at 85° C., hard rubber linings can ruin the processing solution in this manner. This is avoided by filling with a 10% solution of sulphuric and heating the lined container to 85° C. for about 24 hours before using. The same precaution is advisable for electro-plating electrolytes.

With cold solutions used in electro-plating, e.g., acid electrolytes, alkaline cleaners, and acid pickles, the hard rubber linings possess almost indefinite life. With hot solutions, e.g., at 85° C. failure is ultimately by "blistering."

The polythene and rigid P.V.C. coatings have the advantage of more easy application and, the first of these, of better performances with strong nitric acid and with strong cyanide solutions.

For articles such as electroplating racks and jigs, which can be made of brass and coated with hard rubber vulcanised in situ, actually to combine chemically with the metal surface, the ebonite type of covering is ideal. It adheres so that no solution can penetrate between the coating and the brass, and service life is very long. Performance is considered to be superior to that given by the various plastic coatings described above, but the cost of this coating is very much higher, and the coating process is intricate so that it cannot be applied by the user or rapidly by sub-contractors. It is for these reasons that the plastic coatings are so important although for "permanent" jigs, the hard rubber covering will always hold a place.

Other rubber products are available for special purposes. Rubber-resin compounds, with or without inert mineral filling, can be applied by trowelling on hot at 180°/200° C. In solvent solutions they may be brushed or sprayed. As emulsions, they may be sprayed, brushed, dipped or "swilled," e.g. for the insides of tubes. Raw rubber paints can be sprayed and built up into thick coatings, or they may provide the flexible base for chlorinated rubber paints for concrete or metal work. The latter are very resistant to chemical fume, but in themselves generally suffer from poor adhesion and brittleness. An alternative to the raw rubber primer, is the synthetic "etch" primer if the base material is metal.

Phenol Resin Plastics

Phenolic resin compositions are employed for special corrosion resisting coatings on metal work. They are only of limited serviceability because they are thin, and relatively brittle, and exhibit poor resistance to alkali and to strong oxidising agents. Moulded phenolic resin compositions containing inert filler, on the other hand, give excellent resistance to chemicals. They are rarely used as liners, but may have metal reinforcement moulded-in, or be strutted with structural steel work or stays.

Summary

A number of synthetic plastic materials have been established for many years as satisfactory for chemical plant. They have been employed for all types of equipment, large and small, including tanks, towers, digestors, stirrers, pumps, ejectors, cocks, valves, and pipe lines. The longest used material is hard rubber, but of the synthetic resin types, the thermo-setting mineral-loaded phenolics have been used for a diversity of purposes, and have been moulded "seamless" in very large plants. "Haveg" and "Keebush" are proprietary names for a number of special grades of material of this category.

Of the thermoplastic resins, polyvinlidene chloride (proprietary name "Saran") has been extensively used in America, and, in addition to this, polythene and rigid P.V.C., and to a more restricted field, methyl methacrylate, can be employed. Broadly speaking, these materials cannot be employed for such large structures for strength and distortion reasons, but they can serve as liners, and are almost indispensable for connections, including valves and pipe lines.

The plastic linings and coverings applied from sheet, paste, solution or hot dip are invaluable. The sheet materials can be used as more or less permanent linings for inexpensive steel equipment, and the applied coatings for the protection of external surfaces and for ancillary items such as stirring members, jigs, frames, etc. Products of this group thus lie in an intermediate position between all-plastic plant and orthodox paint finishing media of the bitumastic, anti-sulphuric and special synthetic resin types, and with their aid the full advantage of "plastic" plant can be derived.

Gaseous Annealing of Malleable Cast Iron

In his review of the developments in the metallurgy of cast iron, published in our last issue, Dr. Hurst refers briefly to the development of gaseous annealing of malleable cast iron in which he states that the most readily available sources of gas mixtures, for the controlled composition of the furnace atmosphere, are by the partial combustion of fuel gases such as Town's gas, producer gas or carburetted water gas. However, he advises that, while these gases are probably the most convenient for experimental or pilot scale operation, for production annealing re-circulated gases of the self-generated type, in which the desired gas mixture is obtained by reaction of air or steam with the carbon content of the castings, are to be preferred on economic grounds. It is this latter method which is more generally employed when gaseous annealing is applied to the production of malleable iron castings.

Errata

The photograph reproduced on page 297 of the November issue, showing an oil-fired melting unit at the works of The Phosphor Bronze Co. Ltd., was by A. Royce Brown of F. R. Logan, Ltd., and was exhibited at the recent photography exhibition of The Institute of British Photographers. Reference to this was inadvertently omitted from the reproduction.

In the italic preamble of progress in the zinc industry on page 313, November issue, the word "absolute" in the second line should read obsolete.

Copper and Copper Alloys

Technical Progress in 1950

By E. Voce, Ph.D., M.Sc., F.I.M.

Copper Development Association

Although copper has been in use from very early times, continued progress is being made in its metallurgy and that of its alloys. In the various sections of this review of developments during the past year, reference is made to the principal items of interest concerning such subjects as extraction, fabrication, finishing and properties.

BEFORE reviewing in detail the technological progress which has taken place in this mid-century year, it is well to glance back, for a moment, at the conditions which prevailed 50 years ago and to compare them with those of to-day.

In 1900 the electrical industry, by far the largest consumer of copper in the modern world, was in its infancy, and, although the electrolytic refining process had already been established for a decade or more, its output was hardly significant. In fact, the total world production of copper in 1900 was only some 600,000 tons according to statistics published by Knight.[1] By comparison the modern peak production of about 2,700,000 tons per annum attained in the early 1940's is enormous; world output has increased nearly five-fold in 50 years. In those days the principles of flotation, though known, had not been exploited; the now moribund blast furnace vied with the reverberatory in pyritic smelting practice, while the laborious "Welsh process" of converting had not long yielded place to blowing with air.

For the production of brass sheet and strip, the ingots, cast in iron moulds, were tiny by modern standards, and the now almost universal low-frequency electric furnace was unheard of; an integrated plant with continuous casting and fully mechanised rolling equipment, such as that to be described later in this review, could have been no more than a dream. Extrusion had not been applied to copper alloys, and most of the seamless tube of the day was produced from cored billets. Carbide and diamond dies had yet to make their contribution to the speeding of wire drawing, while any machine shop would have appeared to the modern eye as a forest of belts and shafting.

In every year steady progress has been made, and if the contribution of 1950 to be described seems in itself not very great, yet against the perspective of the past half century it surely indicates that an accelerating force is rapidly increasing the pace of technical development in almost every phase of the industry.

The Production of Copper

A Glance Behind the Iron Curtain. Because information from Soviet sources is so scanty, it is interesting to read a brief note[2] concerning the Degtiarka copper mine in the Urals. The surface installations are reported to have been modernised, enabling production to reach 60,000 tons of ore per month. It is said that the deposit is probably the third largest in the U.S.S.R. and that the ore is of very high grade. Extensive exploratory and expansion work is also being carried out in the copper and pyrites mines of Majdanpet in Eastern Serbia, according to Jugoslavian reports.[3] Recent prospecting is said to have shown that these mines, which were thought to be nearly exhausted, may eventually prove more important than the well-known Bor copper workings. Developments apparently planned for this year are to include a flotation plant linked with the mine by a standard gauge railway, and the provision of power from Kostolac.

New Methods of Production. Two important developments in the extraction of copper have been given publicity during the year. These are flash smelting, as now practised in Finland[4, 5] and shortly to be adopted in Canada,[6] and the revised form of the Orford process for the separation of copper from nickel as lately established by the International Nickel Company.[6, 7]

Exact details of the flash smelting plant at Outokumpu[4, 5] are not available, but the essential feature appears to be a tall refractory-lined reaction chamber, near the top of which a mixture of dry, preheated concentrate and suitable fluxes is blown in by a preheated blast of air. The particles burn and melt as they fall and are collected at the bottom on the hearth of a more or less orthodox reverberatory furnace, where they separate into slag and matte in the usual manner. The hot flue gases, rich in sulphur, are used for preheating the charge and air, for raising steam and for the manufacture of sulphuric acid. The process is said to operate smoothly and to be highly economical. It does not necessarily follow, however, that it would prove equally satisfactory for all types of concentrate, a concentrate of fairly high calorific value being clearly desirable.

In the revised form of the Orford process for the separation of copper and nickel, molten copper-nickel matte is cooled slowly to promote coarse crystallization of the individual sulphides. Instead of separating them by gravity segregation during solidification, as in the orthodox Orford process, the new method consists of grinding the solidified mass, and separation of the sulphides by froth flotation. For this purpose the pulp is made alkaline and special agents are used to promote flotation of the copper sulphide and depression of the nickel sulphide. The new process is claimed to be giving very satisfactory results.

Removal of Selenium and Tellurium. During the war the question of the removal of selenium and tellurium from blister and fire-refined coppers became important. Though less deleterious than bismuth, both these impurities are objectionable in copper for, not only are they slightly detrimental to the electrical conductivity, but even when present in small quantities they make welding difficult. With the extension of electrolytic refining, the problem is now of less moment than it was some years ago; nevertheless a report of experimental

work carried out by the British Non-Ferrous Metals Research Association[8] with the object of removing these elements during the converting and fire refining cycles is at once provocative and interesting. While the experiments were conducted on a laboratory scale, the authors express the hope that engineers in charge of converting and fire-refining operations may possibly find ways of applying some of the more successful of the experimental methods they have devised. Among these may be mentioned "selective converting," or cessation of the blow before the whole of the converter charge has been changed to copper, washing the molten blister copper with white metal and, at the refinery stage, the use of a patented alkaline flux under reducing conditions.

The Thermodynamics of Copper Production. Turning to the more theoretical aspects of copper production, Schuhmann[9] has surveyed the thermodynamics of the subject, pointing out the directions in which present knowledge would appear to be adequate and those in which gaps have still to be filled by laboratory research. For the ordinary process metallurgist, the paper is unquestionably difficult to read, but a trained physical chemist in charge of copper smelting and refining operations would find it stimulating. Schuhmann describes in considerable detail the equilibria of slag and matte, and also of the gases, such as sulphur dioxide, oxygen and elemental sulphur, with which they are in contact. He quotes from various sources data from which the equilibrium constants can be calculated for 14 important reactions involved in copper smelting and refining, and gives examples of practical uses to which such constants can be put.

Reviews of Current Practice and Plant Developments. A detailed review by Noakes[10] of copper production in Africa gives an optimistic picture of the industry there. After describing the plants and processes in use by the great copper companies of the Belgian Congo, Northern Rhodesia, Namaqualand and the Transvaal, he points out that everywhere they refuse to be content with their present methods, and through research and sound technical control, are continually seeking fresh developments. It is expected that local user industries, especially electrical firms, will make increasing demands on the output, but "with the enormous reserves of ore available, any such demands can be easily met for many years to come and still leave large quantities of copper for the export trade."

Somewhat broader in scope is a summary by Hill[11] of the cupriferous pyrites industry as a whole. While it gives a useful picture of the occurrence and distribution of pyritic copper ores and of current smelting practice, attention is particularly directed to the recovery of sulphur both by the Orkla process and by roasting techniques which are well known to copper metallurgists.

From Newfoundland comes news of newly revealed deposits of copper, zinc and lead in the Buchans mine,[12] while exploitation of the Canadian copper deposit in the Gaspe peninsula near the mouth of the St. Lawrence will involve the construction of a dam and power station on the Madeleine River and a new road into the mining area.[13]

The Electrolytic Refining of Copper in Britain. Though the electrolytic refining of copper was cradled in this country, economic conditions here have not recently been conducive to the maintenance of such an industry on any considerable scale. In fact until 18 months ago, when Elkington's new refinery came into operation at Goscote,[14] no plant had existed in Britain for many years. Since then, however, McKechnie Bros., Ltd. have announced their intention of commencing the production of cathodes and have stated that they are engaged in experimental work in connection with electrolytic copper powder at Widnes.[15] A small electrolytic refinery is also reported to be under construction in Scotland.[16]

Foundry Practice

General Foundry Procedure. A remarkably comprehensive description of current American methods of control in brass and bronze foundries has been made available by the Society of Automotive Engineers.[17] For so complete a document there are certain conspicuous omissions, notably that of gravity die casting, while in some cases the range of materials available for a particular process is more limited than might be expected.

From the British Non-Ferrous Metals Research Association come a number of important publications. The first of these is a most thorough and able review by Ruddle[18] of the literature concerning the solidification of castings. Though the author finds many inconsistencies, he is able to draw certain tentative conclusions of a general nature, especially in relation to the relative value of different methods of approach to the problem. An appendix comprising a tabular summary of the available data on the thermal properties of metals and mould materials is by no means the least valuable part of the publication.

Ruddle and Mincher[19] have extended the review just described by an experimental investigation of the chilling power of various non-metallic mould materials. Much of the paper is theoretical, but they find that the quantity of heat Q extracted in a time t by unit surface area of the mould under given conditions is defined by the equation

$$Q = q\sqrt{t}$$

where q is a quantity called the mould constant. The relative values of this constant for several different mould materials when pouring copper were found to be as follows :—

	Mould Constant
Dry synthetic sand	244 cal./cm.^{2}/min.$^{\frac{1}{2}}$
Green	258 " "
Dry natural	228 " "
Green	237 " "
Bonded magnesite	354 " "
Bonded silicon carbide	330 " "
Plaster	125 " "

It will be noted that the mould constants for bonded magnesite and silicon carbide were considerably greater than those of the moulding sands, while that of plaster was lower. Thus, in a composite mould, magnesite or silicon carbide could be used to induce a mild chilling effect, while the heat-insulating characteristics of plaster could be used to delay solidification where required. By judicious arrangement of such chills and insulating pads much could be done to achieve the advantages of directional solidification. These conceptions are closely in line with earlier suggestions of Taylor and Wick.[20]

The third of the B.N.F.M.R.A. contributions mentioned above is that by Glaisher[21] on the use of the "metal-mould reaction" to improve the pressure tightness of lead-free gunmetal castings. The paper describes an investigation into the effect of adding phosphorus, as phosphor copper, to degassed metal before pouring, in order to cause a controlled amount of gas absorption by

the reaction of the residual phosphorus with moisture in the moulding sand. By this use of phosphorus in 88 : 10 : 2 and 88 : 8 : 4 gunmetals, the pressure tightness and mechanical properties of disc castings were markedly improved. The idea is based on the fact that degassed lead-free gunmetals are prone to exhibit shrinkage porosity in the form of small interconnected channels, which are broken up by the evolution, during solidification, of a small amount of dissolved gas.

Colton[22] and Swagerman and Leutscher[23] have also published articles dealing in general terms with the melting and casting of copper alloys, while a very readable book by Hull[24] describes the changes that have occurred in the casting of brass and bronze ingots during the past 50 years.

Test Bars for Sand-cast Bronzes and Gunmetals. It is now three years since the issue by the British Standards Institution of their "Code of Procedure in the Inspection of Copper-base Alloy Sand Castings" (B.S. 1367, 1947), in which the "wedge" or "keel" type of separately cast test bar is advocated for general purposes. Lee and Peck[25] have described experiments comparing the B.S.I. keel bar with the well-known D.T.D. type, which is simply a vertically cast cylindrical rod surmounted by a generous feeding head. They conclude that both types of bar are capable of passing present specification requirements, and are sufficiently sensitive to variations in foundry procedure to be suitable for exercising control over melt condition. On the whole, however, the D.T.D. bar appeared to be preferable to the keel bar. (See also references 125 and 126).

A Practical Test for "Melt Quality." O'Keeffe and Taylor[26] have described what would appear to be a simple and effective test for the melt quality of cast bronzes, especially in respect of gas content. The form of the test casting is such that directional solidification occurs from the bottom upwards, while a heat insulated riser ensures thorough feeding. Thus shrinkage porosity is almost entirely eliminated and any unsoundness can be safely attributed to the presence of gas in the melt. Rapid inspection is effected by cutting the feeding head half off and breaking the unsevered portion. Porosity, discernible by discolouration of the fractured surface, indicates that the melt is gassy. It is claimed that this information can be obtained within five minutes of pouring the test block, before the main casting is made.

The Effect of Casting Temperature on 88 : 8 : 4 *Gunmetal.* Ames and Kahn[27] have reported a very extensive series of experiments to explore the effect of variations in casting temperature, with and without phosphor-copper deoxidation, on the tensile strength, ductility, microstructure, density and pressure tightness of 88 : 8 : 4 gunmetal. The authors conclude that neither the degree of superheat nor the temperature at which the metal is withdrawn from the furnace is critical. The pouring temperature, on the other hand, has a profound effect on the mechanical properties and structure. Preferred pouring temperatures range from about 1,050°–1,125° C.

Runners and Risers. Founders in this country recently had the opportunity of viewing a remarkable film prepared by the U.S. Naval Research Laboratory on the gating and running of castings. The substance of part at least of this film, with many stills and diagrams, has now been published in the form of an article by Johnson, Baker and Pellini.[28] Tedds[29] has reported a very similar investigation in which he used glass-fronted plaster moulds into which mercury was poured.

In a comprehensive series of articles Frear[30] discusses in detail feeding systems appropriate for tin-bronze castings, including the use of heat-insulating pads and risers on the one hand and of chills on the other. He gives guidance as to how directional solidification towards the risers may be achieved in practice.

The Casting of High Conductivity Copper. The production of sand castings in copper for high conductivity applications has always presented considerable difficulty. Glaisher[31] describes experiments in which cathode copper was melted under charcoal, to prevent oxidation, and degassed either by plunging marble chips into the liquid or by placing powdered manganese ore at the bottom of the crucible before charging the copper. The deoxidant mainly used was 0·02% phosphorus in the form of phosphor-copper, and conductivities of from 80–97% I.A.C.S. were achieved in most cases, with densities upwards of 8·82 gm./c.c. and tensile strengths well over 11 tons/sq. in.

Die Casting, Centrifugal Casting and Continuous Casting. Barton[32] has written a long series of articles on die design in relation to cost estimation, while Billing and Blanc[33] describe precautions to be taken in the gravity die casting of aluminium bronze in order to ensure the best results obtainable. The die casting of brass has always presented a certain amount of difficulty, mainly owing to the tendency for zinc oxide to build up on the die faces, but the Non-Ferrous Die Casting Co., Ltd.[34] now claim to have developed a satisfactory procedure for the gravity die casting of leaded brass, high-tensile brass and 85 : 5 : 5 : 5 gunmetal.

In a report to the German Foundrymen's Association, Schwietzke[35] emphasises the advantage of centrifugally cast bearings over those made by static pouring methods, while Chase[36] presents a useful resumé of centrifugal casting practice in America. Most of the alloys he mentions are based on copper.

Continuous casting continues to advance in popularity and descriptions of the Scovill[37] and Bristol Brass[38] plants in America have recently been made public.

Fabrication

Modern Rolling Plant and Practice. Brass manufacturers in this country will have read with interest the description by Hoben and Mulvey[39] of the continuous mill recently installed by the Scovill Manufacturing Company at Waterbury, Connecticut. The plant constitutes an integrated unit commencing with the continuous casting of slabs and ending with the despatch of finished brass sheet and strip. It is interesting to note that no hot rolling is included in the schedule, in contrast with British practice where large cast slabs are generally broken down hot.

Melting is conducted in three Ajax-Scomet furnaces of nearly 10 tons capacity and rated at 1,000 kW. each. Each furnace carries three inductor units which can be replaced without interrupting the operation of the furnace. The three furnaces are able to supply over 13 tons of metal per hour to a Junghans-Rossi continuous casting machine, beneath which a flying saw cuts the metal into convenient lengths for breaking down.

Breakdown operations are conducted cold on a two-high reversing mill so highly mechanized that only two men are needed to handle it. The 10-ton slabs are manipulated by pneumatic suction equipment. The four-high run-down mill is likewise fed by means of a suction crane, the product being strip 0·050 in. thick in coils.

A second very similar mill is used for finishing. All the annealing is carried out in four gas-fired furnaces, and highly mechanized spray pickling equipment working at speeds up to 600 ft./min. is incorporated. There are two independent slitting lines for medium and light duty respectively, while a special machine unrolls the coils of strip for inspection.

While there is as yet no comparable mill in this country working on copper and brass, the Institute of Metals discussion of the paper just described tended to show that the use of large integrated mills is likely to spread. On the other hand Underwood[40] maintains that the British industry is admirably served by its smaller and more flexible equipment, which is exceedingly efficient.

The same author[41] has also described in detail considerations involved in the selection of suitable types of cold-rolling mills for different applications.

Polakowski[42] has published two instalments of an illuminating series of articles on the correlation of modern theories of rolling with rolling mill practice. Finding that modern theories tend to be based on an idealised and simplified conception of the rolling process, he proceeds to an analysis of information to be derived from compression tests and pays particular attention to the ratio between the thickness of the metal and arc of contact between the rolls as a factor determining the incidence of edge cracking and crocodiling.

In earlier reviews mention was made of articles by Underwood on the theory and practice of rolling. It is worthy of note that this work has now appeared in book form.[43]

Production of Tube and Wire. The calculation of appropriate sequences of die and plug (or mandrel) sizes in the drawing of tube is by no means a simple matter. Tranier[44] has proposed a systematic method based on the designation of the plug and die sizes by the logarithms of their diameters and the use of logarithmic sectional area ratios for defining the degrees of cold deformation. The author maintains that his system became in practice "a real method of cold drawing, die maintenance and production management." In an addendum to the paper, Voce put forward a modified version of the chart which Tranier employed.

A novel method of producing fine wire has been proposed by the Illinois Institute of Technology.[45] It consists of passing a drawn wire through an electropolishing bath in which the wire serves as the anode and is dissolved away until the desired size is obtained. No details of the process have yet been published, but it would seem that success could only be achieved by very careful control of the operating conditions.

Supplementing earlier trials on a laboratory scale[46] Wistreich[47] carried out a careful investigation of reactive ("back-pull") wire drawing as an industrial technique. He found that the mechanical properties of the wire remained unaffected by the necessarily increased drawing stress, except when this approached the tensile strength of the drawn wire. The saving of power was not appreciable, though there was some evidence of a slight improvement in die life. A modern machine for back-pull wire drawing has been developed,[48] but it would appear to have little advantage in respect of simplicity over the orthodox slip method for copper.

Deep Drawing. Sachs[49] has reviewed the deep drawing and pressing of copper alloys mainly from the point of view of die design. Particularly useful are the many formulae which he gives for determining the blank diameter necessary to produce cups of widely differing shapes, and a critical discussion of the factors determining the maximum reduction obtainable in cupping operations.

Although it does not seem to have been applied to the deep drawing of copper or brass, the "Marform" process[50, 51] appears to be creating considerable interest. Based on the Guerin method of using a rubber bolster in place of the conventional female die, it incorporates a pressure plate which holds the blank in position and prevents wrinkling. The pressure plate itself is operated hydraulically and the pressure applied to it can be varied automatically according to any desired sequence during the stroke of the press. As in the Guerin method, relatively little time is required in setting up the press, and it is claimed that exceptionally high ratios of cup depth to cup diameter are obtainable. Wrinkling is eliminated even from tapered shapes, which are notoriously troublesome from this point of view.

Hot Working. Because the Institute of Metals Symposium on the casting of ingots for working, reported in these pages a year ago, was devoted almost entirely to copper and its alloys, it seems just that the more recent Symposium on the hot working of non-ferrous metals and alloys contained only two papers with a direct bearing on copper. Of these the first, by Cook and Davis,[52] presents an exceedingly comprehensive review of the hot working of copper and its alloys. The paper covers tests of hot-workability and the hot-working properties of a wide range of copper-base materials, with detailed recommendations in respect of permissible quantities of impurities; it concludes with a consideration of the metallurgical features of the hot-working processes most widely used in industry. The second of the two papers mentioned[53] is confined to the hot working of tin bronzes, which are among the more troublesome copper alloys from this point of view. It is concluded that it is quite possible to hot work phosphorised tin bronzes containing up to about 15% of tin, provided that the casting and fabricating conditions are kept under the strictest possible control.

Scheier and Christin[54] have described the application of hard chromium plating for prolonging the life of drop forging dies, especially in cases where the cost of resinking would be high, while Walker[55] gives valuable advice on the designing of such dies. Factors influencing the design of extrusion press dies, particularly in relation to multiple extrusions and the production of unsymmetrical shapes, are discussed by Hemmerich and Arenz[56].

Plating and Finishing

Electroplating. Salauze[57] has critically reviewed a number of modern baths for the electrodeposition of copper, especially from the point of view of eliminating poisonous cyanides from plating shops. For this purpose a number of solutions based on copper oxalate, complex pyrophosphates of copper and an alkali metal, and the addition of sodium sulphamide to copper sulphate are proposed, while for the replacement of sulphate baths, electrolytes containing fluoborates or alkylsulphonates are suggested. Both pyrophosphate,[58] and fluoborate[59] solutions are being increasingly used, and it is claimed that in America the pyrophosphate bath is being applied on a very large commercial scale. With fluoborate solutions, current densities up to 250 amps./sq. ft. can be used, and operation is correspondingly rapid.

In recent years periodic reverse current plating has been evoking considerable interest. The technique as applied to copper plating from cyanide solutions is described by Jernstedt,[60] and by Calistru[61] who claims that bright and firmly adherent deposits of brass as well as of copper can be obtained on iron, steel, zinc and aluminium by using alternating current from the mains.

A general description of the operation of cyanide baths for the electrodeposition of copper-zinc alloys has been given by Graham,[62] who concludes that sludge formation tends to increase as the free cyanide content of the solution decreases and that sludging is associated with the precipitation of zinc-compounds such as zinc ferrocyanide.

The electroforming of copper is dealt with at considerable length by Savage, Fiandt, Reid and Pfefferle,[63] while a new edition of the comprehensive work by Blum and Hogaboom[64] on the principles of electroplating and electroforming has appeared. (See also references 131, 134 and 135).

Stripping Electrodeposits. Turning from the formation of electrodeposits to their removal, Colegate[65] has presented an able review of the methods now employed for stripping. Most of those applicable to copper and brass are based on sodium cyanide in alkaline solution, but mixtures of chromic and sulphuric acids and ammoniacal solutions of ammonium persulphate are also effective.

Chemical Colouring of Copper and Brass. A U.S. patent by Newell[66] claims that a velvety black tenaciously adherent coating is produced on copper and many of its alloys by immersing cleaned parts for from 5–15 minutes in a solution of 2% of sodium N-chlorobenzene sulphonamide and 2% caustic soda in water held at 180° F. Other similar solutions can be substituted.

Tyvaert[67] has described trials of five different solutions for the colouring of brass with tints ranging from light brown to black.

Cleaning and Lacquering. A convenient collection of nearly 500 abstract references to the literature on metal cleaning has been edited by Harris[68] while the suitability of various lacquers for different purposes when applied to metals has been discussed by Tonks.[69] Both these papers are undoubtedly useful for reference purposes.

In cases of poor adherence of enamel to polished brass or bronze, it is suggested[70] that the surface should be roughened by immersion in one or other of the following solutions: (1) sulphuric acid, 1 gallon; nitric acid, 1 gallon; zinc oxide, 2 lb.; temperature, 160°–180° F., or (2) sodium bichromate, 3 oz.; sulphuric acid, ½ pint; water, 1 gallon. The second of these solutions is operated at room temperature.

Chemical Polishing. From the Battelle Memorial Institute comes the news that a technique has been developed for the polishing of copper, brass and many other copper alloys, as well as nickel alloys and aluminium alloys, by dipping in a suitable acid bath.[71] Although the description of this process has figured recently in the technical press, it would appear to be based on a United States Patent which is now several years old.[72] The bath consists of a mixture of nitric phosphoric and acetic acids and is said to be effective over considerable ranges of composition and temperature. It is possible, however, that a number of trials would be needed to ensure satisfactory operation.

Properties of Copper and Copper Alloys

Slow Annealing Coppers. It appears that in America two proprietary brands of copper, known respectively as "Hy-Therm"[73] and "Tensilok,"[74] with delayed annealing characteristics similar to those which are imparted by small additions of silver, are being marketed without price premium over ordinary high conductivity copper. In each case it is claimed that small additions are made of an element or elements which raise the annealing temperature of hard-drawn wire without detriment to the conductivity, but the nature of the additions is not disclosed.

Copper-Manganese-Zinc Alloys. It is well known that the extensive researches of the United States Bureau of Mines on the production and uses of high purity manganese have included the ternary alloys of copper, zinc and manganese. The equilibrium diagram has recently been summarised in a series of isothermal sections of the ternary system at 1,100°, 1,200°, 1,300° and 1,400° F.[75]

Anderson and Jillson[76] claim that alloys of high ductility combined with good tensile strength are obtainable in the following ranges of composition:—

Copper	55–72%
Zinc	10–24%
Manganese	8–31%
Silicon	0·25–1·0%
Aluminium	0·25–0·5%

The iron content should be kept below 0·16% but up to 2% of lead may be added to improve machinability. The tensile strengths lie between 29 and 32·5 tons/sq. in., depending on the exact composition within the range mentioned.

Aluminium Bronzes. It appears that Japanese workers[77] are actively engaged in an intensive study of thermal transformations of the *beta* phase of the copper-aluminium system. The work includes a study of the effects on structure and hardness of the addition of between 2 and 6% of manganese. Klier[78] in America has also investigated the thermal transformations occurring in beta aluminium bronze.

Preliminary investigations are in hand by Panseri[79] on the addition of beryllium to the aluminium bronzes. The most promising compositions so far examined appear to be those containing 5% of aluminium with 1% of beryllium, and 7% of aluminium with 0·4% of beryllium, possibly with additions of nickel. The mechanical properties are claimed to be as good as those of the binary beryllium copper alloys of commerce, while cold working presents no particular difficulty.

A special high-strength aluminium bronze of the 10% aluminium, 5% iron, 5% nickel type, but of carefully controlled composition, has been developed specifically for gas turbine applications particularly in connection with compressor blades.[80] This type of aluminium bronze has also for a number of years been used for moulds in which glass articles are made[81] as well as for press tools.

New Precipitation Hardening Alloys. A relatively new alloy is one in which nickel and phosphorus are added to copper, the ratio of their concentrations being that required to produce nickel phosphide.[82] The solid solubility of this compound in copper varies with temperature in such a way that precipitation hardening effects can be achieved by suitable heat treatment and in the precipitation hardened condition electrical conductivities of about 60% I.A.C.S. are said to be

obtainable. Another new alloy is one which consists of gold, silver, copper and zinc in a wide range of proportions with the addition of from 0·05–1% of beryllium. This material also has precipitation hardening properties and is suitable for jewellery and dental purposes.[83]

Copper in Steel and Cast Iron. A few years ago, enquiries among the British manufacturers of steel elicited the information that little, if any, copper-bearing steel was then being produced in this country. It is interesting to note, therefore, that a recent survey of railroad materials in Germany[84] indicates that a copper content of 0·25% greatly increases the wear resistance of rail steel. A new American stainless steel employs copper as a precipitation hardening element,[85] while the advantages of copper in cast steel[86] and cast irons containing chromium[87] have also been recorded in publications this year. Furthermore, copper-magnesium alloys form an effective means of introducing the latter element into cast iron in order to nodularize the graphite.[88] For such reasons it seems possible that there may be a resurgence of interest in the use of copper in the ferrous field. Moreover, copper clad on both sides with stainless steel, especially in the form of tubing, has been developed in order to combine high thermal conductivity with improved resistance to corrosion.[89, 90]

Joining

Pressure-Welding. The pressure-welding of copper and some copper alloys has been investigated by Davis and Holmes.[91] Pressure-welding involves no melting, but the surfaces to be joined are brought together under sufficient pressure and temperature to cause simultaneous deformation and recrystallization. In joining copper-base alloys by this method, the authors found the most important single factor to be the degree of deformation which occurred in the region of the junction. Deoxidized non-arsenical copper and nine commercial copper-base alloys were tested under a variety of conditions of temperature, pressure and surface treatment, the quality of the welds being assessed by means of tensile tests and metallographic examinations. Taking as the criterion of weldability the minimum deformation required to produce maximum joint strength, the order of merit of the materials tested was: deoxidized copper, 70 : 30 and 80 : 20 cupro-nickel, 93 : 7 and 91 : 9 phosphor bronze, 85 : 15 brass, 60 : 40 brass, silicon bronze, aluminium bronze.

Arc Welding. The application of the inert gas shielded arc technique to the welding of copper has evoked considerable interest, but Marshall,[92] reviewing the development and applications of this process, mentions that argon-arc welds in copper tend to be porous. He states, however, that it may be used successfully for such copper alloys as silicon bronze which contain deoxidants. Marshall's pessimism regarding porosity in copper welds made by the argon-arc method was not shared by the audience he addressed, for, in the discussion, it was maintained that high-quality welds could now be produced in copper by this process. Kelley[93] also reports excellent results with both copper and silicon bronze up to and including thicknesses of $\frac{5}{8}$ in. Either helium or argon may be used.

The application of the carbon-arc process to the welding of copper is described by Child,[94] who points out that, even for this method which does not involve reducing gases other than the relatively harmless carbon monoxide, better results are obtained on deoxidized than on tough pitch copper.

A patent by Rollason[95] claims that the addition of small percentages of manganese or silicon to coated aluminium-bronze welding rods is beneficial in eliminating cracking of the seams at elevated temperatures.

Thermit Welding of Copper. Though there is nothing new in the Thermit process, wherein oxide is reduced to molten metal by reaction with aluminium powder, it does not seem to have been applied to copper welding until recently. Reebel[96] has, however, described a commercial development of the process particularly for joining annealed copper cables.

Glass-to-Metal Seals. The publication of a book on the subject of glass-to-metal seals by so eminent an authority as Dr. Partridge[97] of the General Electric Company is greatly to be welcomed. The book deals comprehensively with all aspects of the sealing of glasses and ceramics to metals, including the methods which involve the use of copper. (See also reference No. 131).

Soldering Iron Tips. The plating of copper soldering bits with rhodium, with or without an intermediate layer of nickel, is claimed to promote long life by increasing the resistance to both oxidation and corrosion by fluxes.[98]

Corrosion

Copper Water Pipes. Of great importance to the plumbing industry is the fact that the B.N.F.M.R.A.[99] have succeeded in defining at least one contributory cause of the pitting type of corrosion which is occasionally encountered in copper water pipes. In comparison with the multitude of trouble-free installations the incidence of pitting is exceedingly small, but it is none the less creditable that clear conclusions have been reached on a matter which has proved baffling for a number of years. A widely published statement by the B.N.F.M.R.A. is couched in the following terms :—

"(1) There is no evidence to establish the superior corrosion resistance of either of the two grades of copper allowed by the British Standards for Light Gauge Copper Tubes for water, gas and sanitation (B.S. 659 : 1944) and for Copper Tubes to be buried underground (B.S. 1386 : 1947). The information available suggests that the two materials—phosphorus-deoxidised non-arsenical copper (B.S. 1172 : 1944) and phosphorus-deoxidised arsenical copper (B.S. 1174 : 1944)—are equally satisfactory in service provided they are both free from the carbonaceous films referred to below.

(2) There is strong evidence that the pitting corrosion of copper cold water pipes sometimes experienced in certain waters is usually due to the presence of carbonaceous films which may be produced inside the tubes by some manufacturing conditions.

(3) Pitting corrosion of copper pipes does not occur in the majority of supply waters in this country, even if carbonaceous films are present.

(4) There is as yet no clear evidence concerning the effect of carbonaceous or other films, originally present, on the serviceability of copper tubes in hot water systems."

The carbonaceous film referred to is very thin indeed and has been attributed mainly to the burning of drawing lubricants while the tubes are being annealed. The films

are cathodic and protective to the underlying copper provided that they are perfectly continuous. They are, however, so fragile that they are easily damaged, and if small patches of bare copper become exposed to one of the few aggressive supply waters in the country, corrosion will be severely concentrated on this small anodic area and local pitting is likely to result.

A full description of the work which led to these conclusions has been presented to the Institute of Metals.[100]

Copper Alloys in Marine Service. A long and detailed account of corrosion problems in sea-water cooling systems of naval vessels, based on practical experience during the war has been published by Slater, Kenworthy and May.[101] The authors describe in turn no less than 11 individual components of the main condensing system of a modern ship, outlining the corrosive influences at work in each case, with an assessment of the optimum materials, mainly copper-base, to use in order to combat them. The chief types of corrosion encountered are stated to be impingement, pitting and deposit attack, and the approximate resistance which the authors ascribe to copper and various copper alloys in respect of these three types of corrosion is reproduced in the accompanying Table. After a full discussion of such contributory factors as the conditions of water movement and aeration, the value of laboratory tests in indicating service behaviour is assessed. It is pointed out that these are now sufficiently reliable to permit their use, not only for preliminary sorting of materials but also for simulating a number of the rarer and more damaging types of corrosive attack. In this way much time and effort can be saved before embarking on expensive trials under actual service conditions.

Aluminium Brass Condenser Tubes. In discussing experiences with various condenser tube materials in an oil refinery, van der Baan[102] singles out aluminium brass as a versatile and economical alloy, but points out that compliance with the usual specifications is not in itself a guarantee of optimum performance. The corrosion resistance appears to depend on other factors not, as yet, known with certainty. Full annealing and the formation of an oxide skin are probably beneficial.

APPROXIMATE RESISTANCE OF MATERIALS TO IMPINGEMENT, PITTING, AND DEPOSIT ATTACK AS OBSERVED IN SERVICE (SLATER, KENWORTHY AND MAY)

Material	Average water speed (ft./sec.) at which risk of impingement attack generally arises under practical conditions	Resistance to pitting	Resistance to Deposit attack
Tough Pitch Copper	6	Moderate*	Moderate
Deoxidized Copper	7	Moderate	Moderate
Arsenical Copper (0·3-0·5% As)			
Admiralty Brass (70% Cu, 29% Zn, 1% Sn)	10	Moderate	Moderate
Naval Brass (60% Cu, 39% Zn, 1% Sn)			
Cupro-Nickel (30% Ni, 0·5-1·5% Mn, 0·4-1% Fe)	15	Good†	Good†‡
Aluminium Brass (76% Cu, 22% Zn, 2% Al, with 0·01-0·05% As)	15	Good/ Moderate§	Very good/ Moderate§
Cast Gunmetal: (88% Cu, 10% Sn, 2% Zn; or 86% Cu, 7% Sn, 5% Zn, 2% Pb)	20	Very good	Very good
Phosphor Bronze (90% Cu, 10% Sn, 0·3% P)	Approaching 20	—	—

* Though attack may be considerable it tends to be widespread and shallow.
† Attack, if any, is usually widespread and shallow.
‡ Cupro-nickel is less affected by decaying organic matter than other materials.
§ Aluminium brass may be badly affected by decaying organic matter.
‖ The authors have had but limited experience of this material in cooling systems.

Physical Metallurgy

Low Temperature Properties. The new book by Teed[103] on the properties of metallic materials at low temperatures is more than a mere compilation of facts and figures, although in this respect it is sufficiently complete to be accepted as an authentic work of reference. The book is published under the authority of the Royal Aeronautical Society, and its keynote is the suitability of the various materials for aircraft construction at high altitudes, where dynamic stresses are associated with sub-zero temperatures. It is encouraging to learn that for the great majority of alloys decrease of temperature improves the mechanical properties, and that this is true of copper and its alloys as a class. The paucity of data on the fatigue properties of copper-base materials at low temperatures emphasises the need for research in this field, though the few figures which the author was able to trace indicate that the fatigue properties, like the tensile and impact strengths tend to improve as the temperature is reduced.

Recrystallization. On a more theoretical note, two investigations of the activation energy associated with the recrystallization of copper have been published. Extending earlier work by Cook and Richards, based on hardness determinations, Thorley[104] accepts the view that recovery and recrystallization are separate processes, and puts forward a method of calculating the activation energy associated with each. In a somewhat similar investigation, using X-ray diffraction methods instead of hardness determinations to assess the extent of recrystallization, Decker and Harker[105] found the activation energies comparable in magnitude with those of Thorley. It is interesting to note that O.F.H.C. copper requires a greater activation energy to cause recrystallization than either the pure metal or the high-conductivity tough-pitch material used by the British workers. This is consistent with the supposition that, in copper of the O.F.H.C. type, even the most oxidizable of the impurities are in solid solution in the copper, where they exert their maximum effect, whereas in the other materials they are either absent or associated with the cuprous oxide phase.

The practical aspects of recrystallization and grain size control in copper and copper alloys have been summarized and discussed by Burghoff[106] with special reference to their effect on tensile properties, creep strength, fatigue strength and susceptibility to stress-corrosion.

Plastic Deformation. During 1949 the American Society for Metals published a series of 18 lectures on the cold working of metals.[107] Together these cover the subject very fully from the theoretical point of view, being concerned more with the mechanism and effects of plastic deformation than with practical cold working processes. Somewhat similar in theme are papers by Swift[108] on the stresses and strains arising in tube drawing, and by McAdam[109] on the effect of temperature on the stress-strain relationships for copper and cupro-nickel. French and Hibbard[110] give the effects of a number of solute elements on the stress-strain curves of copper. It seems unfortunate that these authors attempt to fit parabolic equations to their stress-strain curves by the expedient of drawing *two* straight lines through their double logarithmic plots. Though widely accepted in America, the parabolic relationship between stress and strain commands by no means universal support, and

Palm[111] has shown that hardness, like stress, is related to true strain by an exponential equation which attains an asymptotic stress at large deformations.

Lankford, Snyder and Bauscher[112] make the interesting observation that directional properties arising from preferred orientation may be exploited to advantage in the production of certain unsymmetrical shapes by deep-drawing operations. Hibbard[113] has examined the types of preferred orientation which are developed during the cold rolling of cartridge brass, while Carlson[114] has formulated an etching technique for revealing flow lines in this alloy. Coarse flow lines which may arise, for instance, in cold heading operations are said to be the locale of structural weakness ; this can be eliminated by suitable modification of the heading process.

Oxidation and Electrical Conductivity of Copper. Garner, Gray and Stone[115] have reported a detailed study of the oxidation and reduction of copper, with special reference to the use of this reaction as a catalytic process in chemical syntheses. In the course of this work electrical conductivity measurements were made on thin oxide films, and the effect of the absorption of gases on surface conductivity was studied.

Mention should also be made of work by Rutter and Reekie[116] on the electrical resistivity of copper and aluminium of exceptionally high purity.

Powder Metallurgy

The production of electrolytic copper powder is dealt with in detail by Wranglen,[117] who maintains that a dilute electrolyte in the vicinity of the cathode is conducive to the formation of a powdery or spongy deposit which can readily be disintegrated. More revolutionary in concept is a new Japanese method for the production of pure copper powder by the action of waste sulphite liquor from the pulp industry upon copper sulphate solution.[118] It is suggested that the method may open an entirely new field in the metallurgy of copper. (See also reference No. 15).

Bowden[119] mentions that a plastic based on tetrafluoroethylene gives a very low coefficient of friction against metallic surfaces, and suggests, therefore, that porous metals impregnated with this material should have applications as bearings operating under conditions of deficient lubrication.

Analysis and Testing

Chemical Analysis and "Spot Tests." A most welcome publication is that by Evans and Higgs,[120] who have devised a broad qualitative system of chemical "spot tests" for alloying elements in copper-base materials. The elements which can be detected include aluminium, arsenic, beryllium, cadmium, cobalt, chromium, iron, lead, manganese, nickel, phosphorus, silicon, tin and zinc. Specific and unambiguous results were obtained when the methods described were applied to over a hundred alloys, except that silicon cannot be detected directly when much cobalt is also present.

Goldberg[121] has described the direct colorimetric determination of iron in brass and bronze and claims greater accuracy than that obtainable by conventional methods, while Goetz, Diehl, Harvy and Hach[122] advocate the use of hot concentrated perchloric acid for dissolving sulphide ores in preparation for the iodometric determination of copper.

Advances in Spectrographic Analysis. Spectrographic analysis seems to be extending its scope in connection with copper alloys. Hitherto it has been regarded primarily as a method of determining impurities and alloying elements which are present only in small amounts, but recent advances indicate that it can, to some extent at least, be applied to the determination of the main alloying elements. Thus, using a solution method with porous graphite electrodes, Scribner and Ballinger[123] carried out 100 analyses of a statuary bronze and obtained figures for tin, zinc, lead and nickel consistent to within 3 or 4% of the nominal values. Similar spectrographic methods have been successfully applied to the determination of zinc in brass,[124] a fact which represents a very signal advance.

Mechanical Testing. In a thoughtful review of modern trends towards the standardization of tensile test bars for copper-base alloy castings, Kondic[125] outlines the main requirements of a satisfactory test bar. Whether or not these requirements can be met by any single design of bar remains one of the chief problems of modern research in this field, while effective correlation between the test results obtained on test bars and the properties of the finished casting which they are supposed to represent is still far from achievement. The co-operative investigations of the Association of Bronze and Brass Founders[126] represent one of the best attempts so far made to solve this difficult problem.

Miscellaneous Applications and Processes

Brief reference may be made to certain publications which may prove of interest to users of copper and its alloys in various fields.

In a review of copper and copper alloy springs, Tschanter[127] describes the fatigue behaviour of copper and 24 copper alloys and discusses the effect of temperature on their elastic moduli. The technique of producing printed circuits for electrical instruments is outlined by Hopf,[128] with special reference to the method in which copper foil on a suitable insulating backing is overprinted with an oily "resist," the exposed parts being then etched away with acid. Exceptionally thin copper foil which would appear to be suitable for this purpose is now being produced in this country.[129] A new and speedy method of producing commutators for small electric motors has been described,[130] and an electroforming process for making glass-to-copper seals has been announced.[131] Very thin wires of copper, exploded electrically, are claimed by Conn[132] to provide a light source of high intensity and short duration eminently suitable for photographic exposures, while copper has been used as a ruby colouration for photosensitive glass.[133] Two recent papers[134, 135] have discussed the use of copper rollers for textile printing, and both recommend chromium plating as a protection of the delicate surface against accidental damage, scratching and wear during handling and service. Chromium plating is said to be fairly common practice in the United States and to be gaining favour in this country.

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Staff Changes and Appointments

MR. C. S. GILL, Managing Director of Davy & United Roll Foundry, Ltd., Middlesbrough, a subsidiary of Davy & United Engineering Co., Ltd., has been re-elected Chairman of the Roll Makers' Association of Great Britain for the fifth year in succession. Mr. Gill is also Chairman of the North-East Coast Association of Steelfounders, Employer Representative on the Tees-Side District Advisory Committee of the Northern Regional Board for Industry, Chairman of the Steel Roll Makers' Joint Council, and Member of the Northern Industrial Group.

MR. SAMUEL ERIC OSBORN has been appointed Chairman of Samuel Osborn & Co., Ltd. Other appointments include MR. FRANK ARNOLD HURST as Deputy Chairman and MR. BRIAN CHARLES PYE-SMITH as Director. Mr. Hurst will continue to carry out his duties as Managing Director.

MESSRS. THOMSON MCLINTOCK & CO., of 33, King William Street, E.C.4, and MESSRS. COOPER BROTHERS & CO., of 14, George Street, Mansion House, E.C.4, have been appointed auditors of the accounts of the Iron & Steel Corporation of Great Britain.

DR. R. GENDERS, M.B.E., D.Met., F.R.I.C., F.I.M., consultant metallurgist, has recently changed his address to 40, Grosvenor Gardens, London, S.W.1. Tel. Nos. Sloane 0925 and 6218.

MR. J. P. FERGUSON will be relinquishing his appointment as Scottish Branch Manager of British Aluminium Co., Ltd., which he has held since November, 1946, in order to take up a new appointment in the Head Office of the Company in London as Export Sales Manager. He will assume his new responsibility from January 1 next. MR. M. J. J. RICHARDS, of the Company's Midland Branch Office, has been appointed Scottish Branch Manager in place of Mr. Ferguson and took over responsibility from December 1.

MR. J. W. J. WEBB, Expenditure Assistant to the Chief Financial Officer, Railway Executive, has been appointed Assistant Chief Financial Officer, Railway Executive. He succeeds Mr. V. Radford, who has been appointed Chief Financial Officer, Railway Executive.

MR. D. LACY-HULBERT, B.Sc., A.R.I.C., M.Inst.F., M.I. Plant E., has been appointed Joint Managing Director (Technical) of the Tube Investments subsidiary, Chesterfield Tube Co., Ltd., of Chesterfield. He was formerly Director of Production of the Steel Tube Division of TI, and joined the Chesterfield Tube Co. twelve months ago.

COLONEL J. B. NEILSON, C.M.G., D.S.O., having attained the normal retiring age after 23 years' association with the organisation, will be relinquishing his office of Director and Joint Managing Director of Richard Thomas & Baldwins.

MR. E. S. WADDINGTON, F.S.E., M.Inst.W., A.M.I.E., (S.A.), Ass. I.E.E., Ass. (S.A.) I.E.E., of Industrial Department, Philips Electrical, Ltd., has been appointed by the Institute of Welding to the B.S.I. Technical Committees PSM/8 and PSM/8/1.

MR. A. H. MULDER, who has recently completed twenty-five years' service with Philips Electrical, Ltd., has been appointed Industrial Manager for the Midland Area.

MR. FRED BARKER has been appointed Assistant Manager of Vauxhall Motors' Production Engineering Division in succession to Mr. H. G. Warner, now in the U.S.A. MR. R. L. BLADES, formerly Assistant Production Manager, succeeds Mr. Barker as Production Manager.

MR. WILLIAM PORTON, who has been with General Refractories, Ltd., Sheffield, since 1927 has recently left to take up the position of Secretary to Messrs. Herbert Alexander & Co., Ltd., Engineers, Leeds. Mr. Porton, who was Assistant Cost Accountant at General Refractories, Ltd., served as a lieutenant in the Royal Navy during the war.

WOODS, of Colchester, Ltd., fan manufacturers (an associate company of The General Electric Co., Ltd.), have moved their London offices; their new address will be 58/62, High Holborn, London, W.C.1. Tel. No.: Chancery 5474/8.

The Effect of Surface Finish on the Stress-Corrosion Properties of Aluminium—7% Magnesium Alloy*

By S. E. Hadden, A.I.M.† and E. C. W. Perryman, M.A., A.I.M.‡

(Communication from the British Non-Ferrous Metals Research Association)

The stress-corrosion life of aluminium—7% magnesium alloy sheet, in a susceptible condition, is dependent on the state of the surface. Increase in stress-corrosion resistance results from treatments which introduce into the surface compressive stresses acting in opposition to the tensile stresses operating during stress-corrosion. The production of a magnesium-impoverished surface layer also causes an improvement.

I. INTRODUCTION

DURING work on the stress-corrosion properties of aluminium—7% magnesium alloy, it was found that the stress-corrosion life of material in a susceptible condition was considerably increased by machining or emerying the surface. Following this observation the effect of surface finish was investigated more fully, and the results are given in this paper. In all the experiments described, the aluminium—7% magnesium alloy was deliberately heat-treated to produce a condition which was extremely susceptible to stress corrosion: the results, therefore, do not apply to the commercially produced alloy, which is relatively immune from susceptibility to stress corrosion and has given satisfactory service for many years.

II. EXPERIMENTAL PROCEDURE

A. Materials Used

Analyses of the various batches of aluminium—7% magnesium alloy used are given in Table I and mechanical properties in Table II.

TABLE I.—ANALYSES OF MATERIALS

Batch	Mg %	Fe %	Si %	Mn %	Description
LXU ..	6·7	0·24	0·15	0·30	Commercially annealed 18 S.W.G. sheet
MNY ..	7·38	0·33	0·16	0·20	
NFO ..	6·84	0·20	0·13	0·18	
JQW1 ..	6·90	0·32	0·26	0·31	
KEN ..	7·30	0·30	0·20	0·24	Hard rolled 18 S.W.G. sheet

TABLE II.—MECHANICAL PROPERTIES OF MATERIALS

Batch	Condition*	U.T.S. tons/in.²	0·1% Proof Stress tons/in.²	Elongation % on 2 in.
LXU	3 hours 420° C. + 10% overstrain + 24 hours 125° C. ..	23·1	14·0	17
MNY	ditto ..	22·2	13·2	20
NFO	ditto ..	22·4	12·8	20
NFO	1 week 420° C. + 10% overstrain + 24 hours 125° C. ..	21·7	12·6	20·5

* Treatments at 420° C. were followed by quenching in cold water.

B. Stress-Corrosion Testing

Direct-tensile stress-corrosion tests were carried out using standard 2 in. sheet tensile specimens [B.S. 485 (1934) type A] cut at right angles to the final rolling direction. The specimens were stressed by means of a calibrated spring as described elsewhere[1] and sprayed with 3% sodium chloride solution twice daily. After solution treatment (3 hours at 420° C. followed by quenching in cold water) and overstraining 10% on a 2 in. gauge length, specimens were aged for 24 hours at 125° C.; this treatment gives a material very susceptible to stress-corrosion. All surface treatments unless otherwise stated were carried out as a final operation.

III. RESULTS

A. First Series of Tests (LXU Batch)

Specimens were tested after the surface oxide film produced by the heat treatment[2] had been removed by various methods, some of which produced cold-worked surfaces. The following surface treatments were used:—

(*a*) Emeried parallel to the gauge length, i.e. "longitudinally," under pure benzene with 320 and 500 "Durexsil" papers until all the original oxide film was removed.
(*b*) Polished as for metallographic examination, the final polish being by magnesia sludge in amyl alcohol to avoid etching.
(*c*) Edges only emeried as (*a*).
(*d*) Electrolytically polished in acetic anhydride/perchloric acid mixture.
(*e*) Pickled for 2 minutes in 10% HNO_3 at 60° C.
(*f*) Machined longitudinally.

The above treatments removed the heat-treatment oxide film,[2] but no doubt caused the formation of other types of film, in some cases merely that due to atmospheric oxidation at room temperature.

The results of the stress-corrosion tests at loads corresponding to an initial stress of 4·4 tons/sq. in. are given in Table III.

TABLE III.—EFFECT OF SURFACE CONDITION ON STRESS-CORROSION LIFE OF ALUMINIUM—7% MAGNESIUM ALLOY (LXU). INITIAL STRESS 4·4 TONS/IN.²

Surface Treatment	Life of Each Specimen (days)	Average Life (days)
Untreated (as heat treated)	14, 20, 29	21
Emeried longitudinally	58, 293, 508	286
Metallographically polished (unetched)	71, 225, 327	208
Emeried at edges only	17, 20, 22	20
Electrolytically polished	20, 20, 21	20
Pickled HNO_3	13, 22, A	17½
Machined longitudinally*	>154, >154	>154

Note.—Specimen A had not failed after 323 days but since repetition of this test (Table IV) gave short lives, the result has not been included.

* These tests were carried out on a different batch of material (JQW1) and at a different time. The untreated specimens had an average life of 18 days.

* *B.N.F.M.R.A. Report R.R.3.* 834 *P.* The work described in this paper was made available to members of the British Non-Ferrous Metals Research Association in a confidential report issued in June, 1949.

† Research Assistant, British Non-Ferrous Metals Research Association (London).

‡ Investigator, British Non-Ferrous Metals Research Association (London).

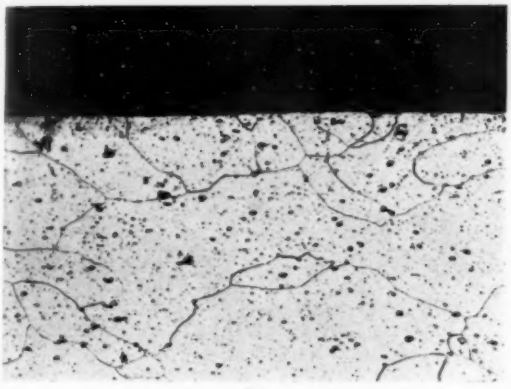

Fig. 1.—Untreated Surface. × 250

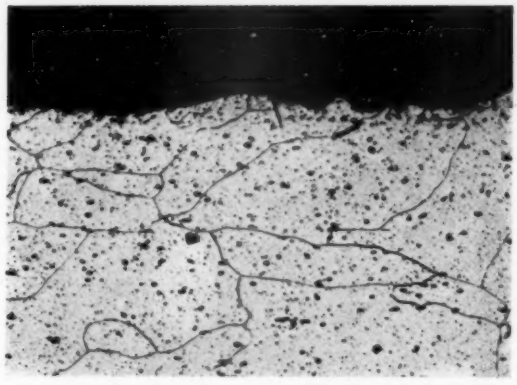

Fig. 2.—Shot-peened surface. × 250

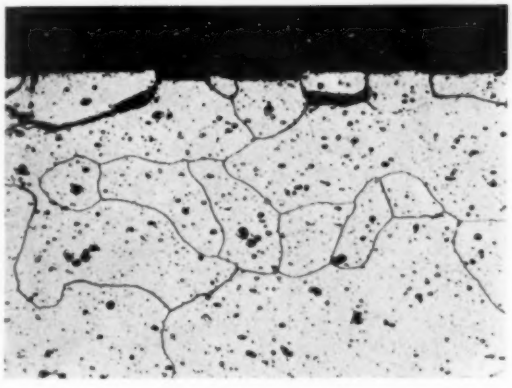

Fig. 3.—Surface pickled in nitric acid. × 2 0

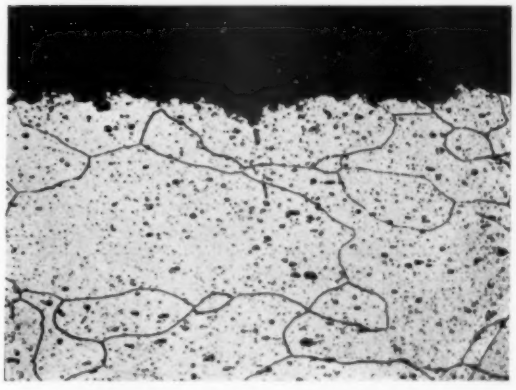

Fig. 4.—Surface wet-blasted. × 250

Figs. 1—4. Aluminium—7% magnesium alloy, homogenised, overstrained 10% and aged for 24 hours at 125° C. Etched in 10% phosphoric acid for ½ hour.

Treatments which cold-worked the surface, i.e., emerying, polishing or machining, markedly increased the stress-corrosion life, which was practically unaffected by emerying the edges only, and by treatments that removed the surface oxide film chemically.

B. Second Series of Tests (MNY Batch)

A different batch of material, given the same preliminary heat treatments and overstrain as before, was tested after the following surface treatments :—

(*a*) Emeried longitudinally (see Section III A).

(*b*) Emeried transversely [as (*a*) but emeried across the gauge length].

(*c*) Shot-peened. 0·026 in. diameter shot was fired from a ¼ in. diameter nozzle 8 in. away from the specimen using a pressure of 5 lb./sq. in. All faces were treated, each for about 20 seconds.

(*d*) Wet-blast. Fine abrasive (No. 4 " Blastyte ") was fired from a ¼ in. diameter jet inclined at 45° and 7 in. from the specimen using a pressure of 35 lb./sq. in., the jet being moved in a longitudinal direction with respect to the specimen, and impinging for 15 seconds on each side. Analysis showed the particles to consist of approximately 95% *alpha* alumina, 2% magnetite, and 2% iron. The treatment produced a smooth matt surface.

(*e*) Buffed. The faces and edges were buffed longitudinally with an 8 in. diameter wheel dressed with Cannings Lustre Tripoli Paste and rotating at 2,850 r.p.m. Overheating was prevented by laying the specimens on a steel slab and allowing plenty of time for cooling between each buffing pass.

(*f*) Metallographic polish (as in Section III A) followed by etching in 10% phosphoric acid for 30 minutes. This etch attacks the *beta* phase produced at the grain boundaries by the heat treatment at 125° C.

(*g*) Electrolytic polish (see Section III A).

(*h*) Pickled for 10 minutes in 5% sodium hydroxide at 60° C. followed by 3 minutes in 10% sodium hydroxide at 60° C.

(*i*) Pickled for 1¼ minutes in a solution consisting by volume of one-third water, one-third concentrated nitric acid, and one-third concentrated hydrochloric acid, with 2% of concentrated hydrofluoric acid added.

(*j*) Pickled for 8 minutes in 10% nitric acid at 60° C. (*c.f.*, 2 minutes in the first series, Section III A).

(*h*) Chamfered edge (round). Corners were slightly rounded with a fine file and 400 Durexsil emery before heat treatments and overstraining. The radius of the rounded corners was about 1/100 in. Otherwise the specimen surfaces were untreated.

(*l*) Chamfered edge (flat). Corners were filed and

emeried flat at 45° to the surfaces before the heat treatments and overstraining.

The pickling, emerying and buffing treatments removed the dark oxide film due to heat treatment. Shot-peening and wet blast appeared to disintegrate this film but not to remove it.

Microscopical examination of the different surfaces showed that in all cases the grain boundary *beta* network extended to the treated surface (see Figs. 1, 2, 3 and 4), but it must be borne in mind that a flowed layer may be present which would not be seen by microscopical examination of the cross-section. Shot-peening and wet-blasting deformed the surface crystals; the deformation was deeper but on a finer scale after wet-blasting than after peening. No deformation could be seen after emerying or buffing. The chemical treatments produced no peculiar surface effects, except nitric acid which produced some intercrystalline attack (see Fig. 3). After etching with phosphoric acid or pickling in sodium hydroxide the grain boundaries were visible.

Results of stress-corrosion tests carried out at an initial tensile stress of 4·5 tons/sq. in. are given in Table IV. Some results are also given for an initial tensile stress of 7 tons/sq. in.

TABLE IV.—EFFECT OF SURFACE CONDITION ON STRESS-CORROSION LIFE OF ALUMINIUM—7% MAGNESIUM ALLOY (MNY)

Surface Treatment	Initial Stress tons/in.²	Life of each Specimen (days)	Average Life (days)
Untreated	4·5	2, 2, 4, 4	3
Emeried longitudinally	4·5	20, 21, 23, 60	31
Shot-peened	4·5	8½, 11, 11, 16	11½
Emeried transversely	4·5	4, 4, 4, 5	4
Wet-blasted	4·5	11, 82, 136, > 64(a)	> 73
Buffed	4·5	11, 11, 21, 60	26
Chamfered edge (round)	4·5	2, 6, 8½, 8½	6
Chamfered edge (flat)	4·5	5, 5, 6, 19	9
Metallographically polished and etched	4·5	1, 2, 4, 6	3
Electrolytically polished	4·5	2, 2, 2, 3	2
Pickled–sodium hydroxide	4·5	½, ½, 2, 2	1
Pickled–mixed acid [see III B (i)]	4·5	½, ½, ½, ½	½
Pickled–nitric acid	4·5	2, 2, 4, 5	3
Untreated	7·0	½, ½, ½, ½	½
Emeried longitudinally	7·0	½, ½, ½, ½	½
Shot-peened	7·0	2, 2, 2, 2	2

Specimens with lives assessed as ½ day failed at some unknown time during the night after setting up.
(a) The fourth specimen had not failed at 64 days but was then spoiled.

The results in Table IV, confirm that treatments which cold-work the surface tend to lengthen the life, while those which do not, have little effect. Emerying transversely had much less effect than emerying longitudinally. In tests with an initial stress of 7·0 instead of 4·5 tons/sq. in., emerying or peening had little effect. This variation of the effect of emerying with the stress applied was also noticed in a series of tests using a further batch of material (NFO). Specimens with untreated surfaces (as heat-treated) tested at 3·8 and 4·5 tons/sq. in. failed with average lives of 17 and 9 days respectively. Similar specimens which had been emeried longitudinally after heat treatment failed at the same stresses, with average lives of 46 and 10 days respectively. This relationship between applied stress and increase of life due to treatments which cold-work the surface will be referred to later.

C. Third Series of Tests (KEN Batch)

One explanation of the increased life due to cold-working the surfaces is that compressive stresses are set up in the surface, which oppose the applied tensile stress. Such compressive stresses should be relieved by further heat treatment. To test this possibility specimens were emeried at various stages during their preparation. Details of the specimens in this series and the results, are given in Table V.

TABLE V.—EFFECT OF EMERYING, AT VARIOUS STAGES OF THE PREPARATION, ON THE STRESS-CORROSION LIFE OF ALUMINIUM—7% MAGNESIUM ALLOY. (KEN BATCH). INITIAL APPLIED STRESS 4·4 TONS/IN.²

Group	Treatments (in chronological order)	Individual Lives (days)	Average Life (days)
(a)	3 hours 420° C. + 10% overstrain + 24 hours 125° C.	13, 21, 21, 24, 57	27
(b)	Emeried longitudinally + treatment (a)	21, 28, 39, 39, 118	49
(c)	3 hours 420° C. + longitudinal emerying + 10% overstrain + 24 hrs. 125° C.	55, 99, 141, 152	112
(d)	Same treatment as (a) + longitudinal emerying	56, 108, 119, 133, > 285	> 140

It is clear that the increase in stress-corrosion life is very much less when emerying is carried out prior to solution treatment at 420° C. than when it is carried out after solution treatment. This could be due to relief of a surface compressive stress set up by emerying.

D. Effect of a magnesium impoverished layer on the stress-corrosion properties of aluminium—7% magnesium alloy

It was perhaps surprising that heating for 3 hours at 420° C. did not eliminate the effect of longitudinal emerying on stress-corrosion life (Table V). Further specimens were heated for a week at 420° C. after longitudinal emerying and were found to have a life of 59 days, i.e., rather longer than that of similar specimens heated for only 3 hours at 420° C. It seemed likely that this effect could be due to the loss of magnesium from the surface layers, for Vosskühler[3] has reported such losses from aluminium—8% magnesium alloys heated for 24 hours in a fused nitrate bath at 430° C. and has claimed that increased resistance to stress-corrosion resulted. The following experiments were made to test this possibility.

The existence of an impoverished surface layer after heat treatment at 420° C. for 1 week was shown by measuring the lattice parameter of successive layers near the surface. Back-reflection scanning X-ray photographs, using unfiltered cobalt radiation and an exposure time of 20 milliampere hours, were taken from specimens solution treated at 420° C. for 3 hours and 1 week, respectively, after successive pickling in the solution of mixed acids described in Section III B (*i*). The results are shown in Fig. 5. The lattice parameter for material treated at 420° C. for 3 hours did not change as the surface layers were removed. With material treated at 420° C. for one week, however, the lattice parameter near the surface was lower than the value for material given the 3 hour treatment at 420° C., and progressively approached this value as the surface layers were removed, becoming equal to it at 0·0044 in. below the surface. From the lattice parameter curves given by Lacombe[4] or Hume-Rothery[5], these results show that the magnesium content just below the surface was reduced by about 1·3% magnesium after treatment for 1 week at 420° C. (No value for the actual surface is obtainable since the depth of penetration of the X-radiation is about 0·0008 in.).

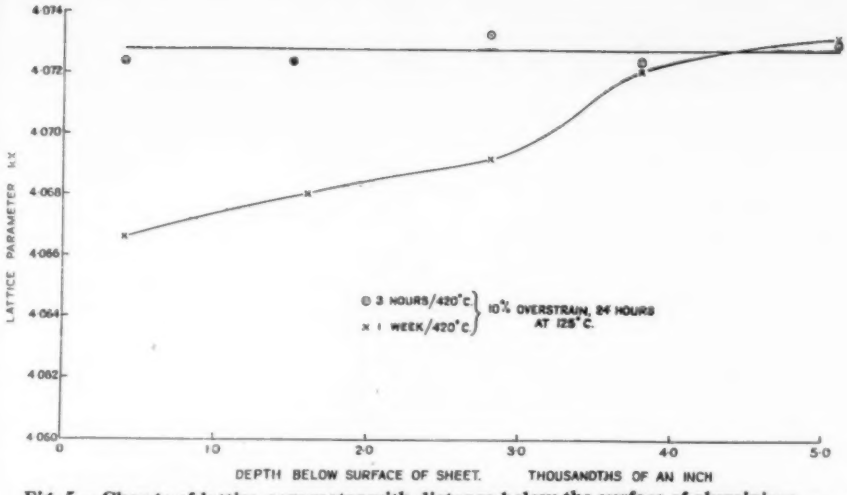

Fig. 5.—Change of lattice parameter with distance below the surface of aluminium—7% magnesium wrought sheet after short and long periods of solution-treatment at 420° C.

Results of stress-corrosion tests carried out at an initial applied stress of 4·5 tons/sq. in. are given in Table VI. The tests in the two sections of Table VI were done at different times.

TABLE VI.—EFFECT OF HEAT TREATMENT AT 420° C. FOR 1 WEEK ON STRESS-CORROSION LIFE OF ALUMINIUM—7% MAGNESIUM ALLOY (NFO BATCH)

Group	Treatments and Order in which given	Individual Lives (days)	Average Life (days)
(*a*)	3 hours 420°C.+10% overstrain+125°C. 24 hours	7, 10½, 10	9
(*b*)	1 week 420°C.*+10% overstrain+125°C. 24 hours	27, 49, 71	49
(*c*)	As (*b*)+longitudinal emerying	16, 17, 30	21
(*d*)	1 week 420°C.*+10% overstrain+125°C. 24 hours	43, 51, 88	63
(*e*)	As (*d*) but pickled to remove 0·001 inches from surface	3†, 22, 22	22

* These specimens had already received 3 hours at 420° C.
† Ignored in calculating average.

The results (*a*), (*b*) and (*c*) in Table VI show that the 1 week's treatment at 420° C., which produced a surface layer impoverished in magnesium, increased the stress-corrosion life, but that after a final emerying treatment the increase in life was much less marked. This is presumably due to partial removal of the magnesium-impoverished surface layer. Support for this is given by the decrease in life brought about by pickling away some of the impoverished surface layer [see groups (*d*) and (*e*) Table VI].

IV. SUMMARY OF RESULTS

The surface treatments can be divided into the following groups :—

(*a*) Machined, longitudinally emeried, wet-blasted, buffed, shot-peened and metallographically polished without etch. All these treatments cold-worked the surface and caused long lives.

(*b*) Untreated, electrolytically polished, pickled in NaOH, pickled in HNO_3, pickled in solution of mixed acids, and metallographically polished and etched. All these specimens had work-free surfaces and short stress-corrosion lives.

(*c*) Emeried transversely. This treatment cold-worked the surface but the life was only slightly greater than that of untreated specimens.

(*d*) Emeried at edges only. This treatment did not significantly affect the life.

(*e*) Chamfered edges. This treatment resulted in a moderately increased life.

(*f*) Surface layer impoverished in magnesium. This treatment resulted in an increased life which, however, was decreased by longitudinal emerying.

The variation in average lives of similarly treated specimens in different experiments is due partly to a difference in stress-corrosion susceptibility of the various batches of material, and partly to the fact that the tests were carried out at different times and, hence, with varying average relative humidities, a factor which has been shown[1] to have a pronounced effect on the results of salt spray stress-corrosion tests.

V. DISCUSSION OF RESULTS

A. Effect of Cold-Work

Two possible reasons suggest themselves for the increased life of specimens with a cold-worked surface : (*a*) production of a flowed layer and (*b*) the production of a surface compressive stress. For convenience these two possibilities will be considered separately.

(*a*) *Flowed Layer Theory*

Cold-working the surface may cause solid solution to flow over the *beta* precipitate at the grain boundaries, thus protecting it from the corrosive medium. This would tend to delay intercrystalline corrosion which is the first stage of the stress-corrosion process.[6]

It is not possible to decide whether this view is correct by examining microsections as the thickness of such a flowed layer would be too small to be detected. This theory, however, fails to explain the difference between the lives of specimens with transverse and longitudinally emeried surfaces.

(*b*) *Compressive Stress Theory*

Other workers[7,8] have shown that shot-peening increases the stress-corrosion resistance of magnesium-aluminium-zinc alloys and have suggested that the shot-peening induces compressive stresses in the surface. In the case of shot-peening the compressive stresses will be in all directions but can be resolved into two directions, transverse and longitudinal. Longitudinal stresses will oppose the applied tensile stress and so decrease the effective stress on the surface layers. During the initial stages the stress-corrosion process will hence be governed by this reduced stress. Transverse stresses such as are produced by transverse emerying will have little effect in reducing the applied stress.

As the initial applied stress is increased, in constant-load direct-tensile stress-corrosion tests, the life decreases

TABLE VII.—THE EFFECT OF BATCH OF MATERIAL AND INITIAL STRESS ON THE STRESS-CORROSION LIFE OF EMERIED AND SHOT-PEENED SPECIMENS

Batch	Initial stress tons/in.²	Life (days)		
		Untreated Specimens	Specimens Emeried Longitudinally	Specimens Shot-peened
NFO	3·8	13, 17, 22 (17)	42, 43, 53 (46)	—
NFO	4·5	7, 10½, 10 (9)	10, 10½, 10½ (10)	—
MNY	4·5	2, 2, 4, 4 (3)	21, 21, 23, 60 (31)	8½, 11, 11, 16 (11½)
MNY	7·0	½, ½, ½, ½ (½)	½, ½, ½, ½ (½)	2, 2, 2, 2 (2)

Figures in brackets are mean lives.

rapidly at first and then progressively less rapidly. The form of this curve is such that a given reduction in the applied stress will cause a greater lengthening in life for a low initial stress than for a higher stress (see Fig. 6). Certain results, summarised in Table VII, show that the increase in life due to emerying and shot-peening depends on the initial stress in this way, as would be expected if these treatments introduced a surface compressive stress opposing the applied tensile stress.

Moreover, when specimens were heat-treated at 420° C. after emerying, the stress-corrosion life was much less than with specimens emeried after the heat treatment (see Table V). Surface compressive stresses would be relieved by subsequent solution treatment and hence these results support the theory that compressive stresses cause the longer life.

It should be noticed that a metallographic polish without etch increased the life, but that etching after the polishing restored the short life (Tables III and IV). It must therefore be assumed that the surface layer containing the compressive stress was very thin, being removed by 30 minutes immersion in 10% phosphoric acid. It has already been shown, during the tests on specimens with magnesium-impoverished surface layers, that thin surface layers with properties different from those of the core have a great effect on the stress-corrosion life.

It should be pointed out that treatments which cold-work the surface can have two opposing effects: (i) a beneficial effect due to compressive stresses, and (ii) a detrimental effect due to increase in precipitation of the *beta* phase if ageing occurs subsequently. The overall effect in any instance will depend on the balance between these two factors. In the tests described in the present report the beneficial effect has usually predominated since the *beta* phase was already heavily precipitated at the grain boundaries in all the specimens by overstraining 10% before ageing at 125° C. for 24 hours. It is possible, as shown by Edeleanu,[9] for emerying to decrease the stress-corrosion life, if ageing occurs after emerying.

B. Specimens not Cold-Worked

Minor differences in the life of specimens not cold-worked may possibly be explained by differences in the oxide films present before corrosion. It is likely that different films will modify the initial rate of inter-crystalline attack to different degrees.

VI. CONCLUSIONS

(*a*) Suitable surface treatments after ageing, e.g., longitudinal emery, wet-blast, buffing or metallographic polish without etch can considerably increase the stress-corrosion life of aluminium—7% magnesium alloy. The

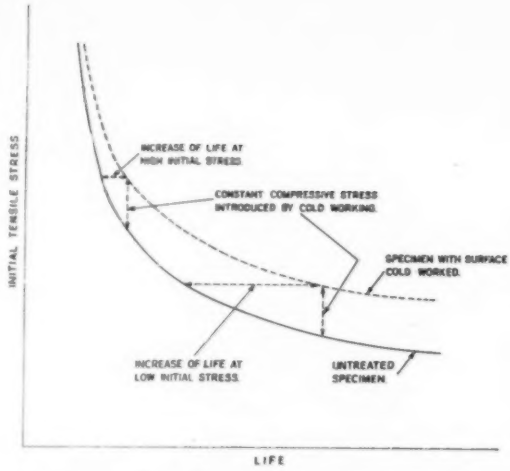
INITIAL TENSILE STRESS
INCREASE OF LIFE AT HIGH INITIAL STRESS
CONSTANT COMPRESSIVE STRESS INTRODUCED BY COLD WORKING
SPECIMEN WITH SURFACE COLD WORKED
INCREASE OF LIFE AT LOW INITIAL STRESS
UNTREATED SPECIMEN
LIFE

Fig. 6.—Theoretical load/life curves for stress corrosion specimens with untreated and cold-worked surfaces.

effect produced can be ascribed to compressive stresses produced in the surface, acting in opposition to the stresses applied during stress-corrosion. The increase in life conferred by longitudinal emerying or shot-peening becomes small at high initial stresses. The effect of emerying varies with the batch of material used as well as with the initial stress.

(*b*) Small differences in the stress-corrosion life occur when the heat-treatment oxide film is removed by chemical means.

(*c*) The presence of sharp corners somewhat decreases the stress-corrosion life, probably because local stress concentrations accelerate the onset of stress-corrosion.

(*d*) The stress-corrosion resistance can be increased by producing a thin magnesium-impoverished surface layer.

ACKNOWLEDGMENTS

The work recorded in this paper was undertaken as part of a research on the stress-corrosion of light alloys carried out for the Principal Director of Scientific Research (Aircraft), Ministry of Supply.

The authors wish to thank the Chief Scientist, Ministry of Supply and the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish this paper.

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Nu-Way Heating Plants, Ltd.

PLANNED to serve London, Home Counties and Hampshire, Nu-way Heating Plants, Ltd., have opened their London Office at 110/111, Strand, W.C.2. Tel.: Temple Bar 5671 (3 lines). It is hoped that this central position, adjoining the Savoy Hotel, will be found especially convenient to intending visitors from overseas. The Head Office and modern works are, of course, situated at Droitwich.

The New 42-in. Slabbing Mill at Shotton

Further Progress at the Hawarden Bridge Steel Works

Originally envisaged in 1939, a scheme of development at the works of John Summers and Sons, Ltd. has proceeded steadily in well defined and planned stages. Since 1944 it has been pushed ahead more vigorously and much additional plant has been installed and brought into operation. Most recent of these installations is a 42 in. reversing slabbing mill, which is expected to have an output of 20,000 tons/week, the main features of which are described in the present article.

The slabbing mill and its control cabin. Notice how this, the offside of the mill, is kept entirely clear for roll-changing operations.

THE scheme of development now in hand at the Hawarden Bridge Steel Works of John Summers and Sons, Ltd., was originally envisaged in 1939 when the famous strip mill was first put into service, its main purpose being to increase the capacity for producing steel sheet and wide strip with continual improvement in the technique of the manufacturing processes involved.

The scheme proceeded steadily in well defined and planned stages until 1944 when it was pushed ahead more vigorously and much additional new plant installed, notable among which are extensions to slab furnace capacity, an additional annealing plant, new soaking pits, an 80 in. wide four-high reversing cold strip mill, an 80 in. four-high skin pass mill, the addition of a fourth stand to the 56 in. wide tandem cold mill, an 80 in. coil slitting and trimming line and a 74 in. wide rotary shear line.

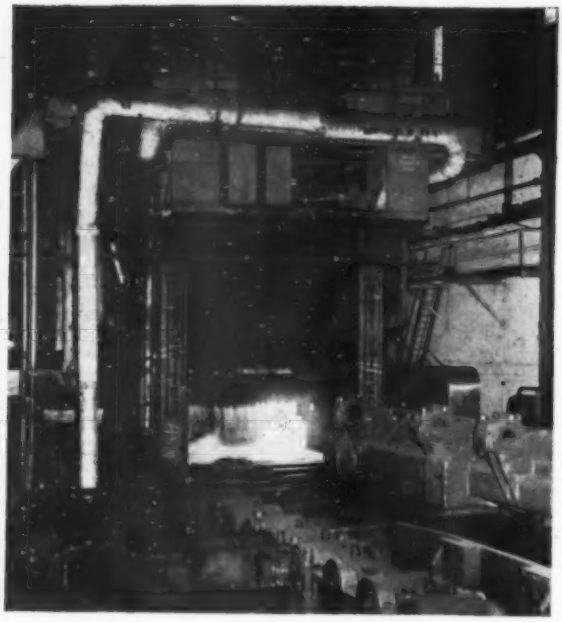
A further important step forward has been made, by the installation of a new 42 in. × 8 ft. reversing slabbing mill with a lift of 61 in. designed to handle ultimately a tonnage virtually double that of the present Shotton plant. This Davy-United mill, supplied complete with a slab shear of 900 tons blade load, is now working up into full production, and is at present rolling 8 ton ingots. It will, however, shortly be handling 12½ ton ingots and has in fact been designed to accept a maximum ingot size of 15 tons against the future completion of extensive enlargements to steel making capacity which this steel firm has in hand. With this largest size of ingot the mill is expected to reach easily its projected weekly output of 20,000 tons.

The slabbing mill previously in service at Shotton could produce slabs only up to 40 in. in width. When these slabs were fed into the hot strip mill, which is a 56 in. wide mill, the first operation had to be a broadsiding operation to bring the slab up to the required maximum width before passing it on to the remaining stands of the 8-stand hot mill line. The new slabbing mill is able to produce a slab up to 55 in. in width, by up to 7 in. in thickness, which thereby effectively eliminates the necessity for this previous broadsiding operation and thus enables the hot mill to operate as a fully continuous line.

Close collaboration between John Summers and Sons, Ltd. and Davy and United Engineering Co., Ltd., has covered not only general aspects but also particular features of the design of various units and the success with which it has operated has undoubtedly contributed largely to the smooth, trouble-free manner in which this new mill has gone into service. A factor which governed primarily much of the designing on the job was that the mill had to be put down on existing foundations, on which a previous slabbing mill of American manufacture had operated. In addition it was decided that the mill should be arranged for driving from the existing three-cylinder horizontal steam engine and this too materially influenced design considerations.

The mill itself has roll housings of the closed top type, with minimum cross sectional post areas of 550 sq. in.; they have been specially designed to accommodate the necessary maximum lift on the top roll of 61 in. The housings are also constructed to allow roll changing to be effected by the axial withdrawal of both rolls simultaneously and to carry a breast and first roller at each side of the mill. Cast steel chocks are used and are fitted with bearings of the flood oil lubricated type for the roll necks, a notable feature of the design of this mill.

The housing screws are of forged special 0·5% carbon steel and have a diameter of 16 in. They work in phosphor bronze screwboxes fitted into seatings in the housing tops secured with keep plates and stud bolts. Screwdown gear is supplied with twin-motor electric drive from two 150 h.p. motors which give a screwing speed of 250 in. per minute. Both the screwdown and



The last edging pass. The maximum lift of 61 in. is a feature of this mill.

index gear, which is also fitted to the housings, are designed for the maximum required lift of 61 in., the position of the top roll being shown on a dial indicator with two moving fingers to indicate the slabbing and edging passes. There are two additional indicators mounted on the end of each screw which register fine settings down to $\frac{1}{16}$ in., these indicators being illuminated and made visible to the mill operators.

Top roll balance is provided hydraulically from two hydraulic cylinders carried in the housing tops and having 12 in. diameter Fescolized cast iron rams made for an hydraulic working pressure of 700/750 lb./sq. in. The ram of each cylinder is connected by crosshead, levers and links to two balance beams running across between the housings and secured to the top rider chocks, the balancing effort being transmitted to the carrier chocks by special bolts which are removed when roll changing.

The mill itself makes use of the already existing steam engine drive which is provided by a three-cylinder horizontal steam engine of Scott & Hodgson manufacture with a nominal horse-power of 4,000 at 55 r.p.m. and a maximum horse-power of 5,300 at 105 r.p.m. Though it has a number of years of hard service behind it this engine's performance under this particularly exacting duty is quite first-class, providing a reserve of power adequate for all the new mill's needs, with positive and instantaneous reversals.

The drive is transmitted to the reduction gear unit by flexible coupling while a further coupling of the same type connects the gear box to the new pinion housing which has been supplied with the mill. This pinion housing, which is of particularly massive proportions, is of the totally enclosed type with spray lubrication to the pinion teeth. The pinions are 57 in. pitch circle diameter with 71 machine-cut double-helical teeth of 50 in. face width; they are built up with 2½% nickel-chrome-molybdenum steel rims shrunk on to 0·35% carbon steel arbors. From the pinion housing the drive is transmitted to the mill by coupling spindles provided with couplings of the universal jaw-end type arranged for lubrication from the central system at the pinion housing end and at the mill end for grease-gun lubrication by means of Tecalemit nipples.

Hydraulic balance is provided for both top and bottom spindles, one hydraulic cylinder mounted on the roll housing top providing balance for the top spindle with two further cylinders for the bottom spindle. These hydraulic cylinders are served from the same hydraulic system as provided for the top roll balance gear with suitable isolating valves interposed which can lock the hydraulic fluid and hold the spindles in position during roll changing.

Due to the very restricted lateral space available at the right hand ingoing side of the mill the manipulating and tilting gear had to conform to a special and very novel design conceived originally by Summers' engineering staff. The manipulator itself is basically of the electrically-operated universal side-guard type which has been a feature of Davy-United design in mills of this type during recent years. A notable feature of this design is that all actuating mechanism is positioned entirely on the main drive side of the mill, thus leaving the other side completely free for roll-changing operations.

From the mill the long slabs travel down the continuous roller table to the open-sided up-cutting hydraulic slab shear which forms the other major unit of this new mill installation. This shear, is capable of cutting slabs 55 in. wide by 5 in. thick or of equivalent section up to a maximum thickness of 8 in. It has a maximum blade load of 900 tons with a maximum stroke

The open-sided up-cutting hydraulic slab shear. With a maximum blade load of 900 tons, and a maximum stroke of 12 in., the shear can cut slabs 55 in. wide by 5 in. thick, or of equivalent section up to 8 in. thick.

of 12 in. The blades are 60 in. long. Having a main ram diameter of 25 in. and employing a working pressure of up to 2 tons/sq. in., the shear is capable of making three cuts per minute continuously. Again, this major item of equipment was required to fit on to previous foundations.

The shear is operated by a hydraulic service consisting of an electrically-driven horizontal three-throw hydraulic pump and a 100 gallon air-loaded hydraulic accumulator designed for a maximum working pressure of 2 tons/sq. in. The pump, which is driven by a 250 h.p., 975 r.p.m. motor, through a totally-enclosed single-reduction gear unit, runs at 150 r.p.m. and has three rams each of $2\frac{1}{4}$ in. diameter with a 12 in. stroke.

These then constitute the main features of this new plant which has an obvious importance in the drive to step up the volume and efficiency of British steel production. Altogether the plant represents approximately 1,250 tons of new machinery and this very considerable weight of equipment is in some ways a measure of the efforts being made to increase the facilities available for production at Sholton.

CURRENT LITERATURE

Book Reviews

GALVANIZING (HOT-DIP)

By Heinz Bablik. Third Edition. Translated by Clive A. Bentley. 502 pp. 1950. Published by E. & F. N. Spon, Ltd. Price 70s. net.

A NEW edition of this well-known book on galvanizing will be welcomed by all those concerned in any way with hot-dipped zinc coatings. The text has been revised and certain sections brought up-to-date. The sections on electro-galvanizing, sherardising and spraying, included in the 1936 edition, have been omitted but the book has nevertheless increased slightly in size.

The treatment follows, in general, that of the earlier editions. A discussion of the scaling of steel (12 pp.) is followed by a long discussion of pickling theory (83 pp.) and pickling practice (35 pp.). A discussion of fluxes and fluxing occupies 20 pages and is followed by 207 pages on the theory of galvanizing. The actual technique of various galvanizing processes, sheet, tube, wire and general galvanizing, is dealt with in 60 pages under galvanizing practice, which includes a further 34 pages devoted to a good account of bath-heating practice. The book ends with 24 pages on the subsequent treatment and testing of the coating. The theoretical and experimental aspects of galvanizing thus receive far more attention than the practical side of the subject. It is a matter of opinion, perhaps, whether this tendency has not been overdone. In the section on scale it is surprising that there is no reference to L. B. Pfeil, especially since the iron-oxygen diagram included in Fig. 1 is actually due to him.

Although the development of strip rolling is frequently referred to, the section on pickling does not include a description of the continuous pickling of hot-rolled strip. In such installations pickling conditions are different from those of sheet pickling and the problem of fume (pp. 133–136) is completely solved.

The hardness values given in Table 101 (p. 255) are somewhat surprising. One would expect a "martensitic" steel containing 0·78% C., to have a greater hardness than 270 Brinell. The same steel in the annealed, pearlitic, state is said to have a hardness of 59 H_s—a value more typical of completely decarburised and pure iron.

Corrosion is dealt with as a sub-section of galvanizing theory. This subject deserves a separate chapter placed later in the book. Dr. Bablik does not appear to believe that zinc provides electro-chemical protection (p. 311); he says (p. 313) that uncoated spots "will rust without hindrance" and that the zinc "cannot give protection at a distance." These views will surprise those who have read the work of C. E. Richards and others.

Dr. Bablik is in error when he states (p. 314) that the probable lives of coatings calculated by Dr. J. C. Hudson should be trebled. In the original paper (p. 204, para. 2) Dr. Hudson makes it quite clear that these estimates are calculated from the corrosion of pure zinc assuming a coating on "ordinary commercial galvanized sheets" of 0·75 oz. per sq. ft. *of surface*. This is quite a reasonable value and the estimates should *not* be trebled.

The figures for antimony in zinc given in Table 165 (p. 345) may mislead the reader. These values are for *lead* and not antimony. Under "new developments" in bath heating (p. 415) no mention is made of the possibilities of induction heating as described by Tama. The description of the lead-zinc process for sheets (pp. 417–422) would have been improved by including a discussion of a mechanised unit employing this process instead of, or in addition to, the old fashioned and laborious hand-dipping process described on p. 418.

The following may be quoted as examples of the numerous errors and omissions which have been noticed. Fig. 282 is given without the magnification, obviously very high, and it may mislead the reader. The magnification, given for Fig. 284 seems wrong while that of Fig. 290 is definitely wrong; the latter is Fig. 10 in the original article by Fred Crapo where the magnification is given as ×520, not ×1200. The coating weights given at the bottom of p. 448 are ridiculously high. Table 207 (p. 459) contains two errors. Pellowe is wrongly spelt in two places and "short period corrosion" (p. 481) should be followed by "resistance." The reduction of iron to the ferrous state with zinc chloride (p. 490) presumably refers to stannous chloride.

"Examination of the coating" is dealt with in the last 15 pages and is, perhaps, the weakest section of the book. Electrolytic zinc coatings are not necessarily "much thinner than hot galvanized ones" (pp. 365 and 486). The reviewer cannot accept the statement that the addition of Sb, As, etc. to stripping solutions "offers no practical advantages whatever," and the B.N.F. jet test (p. 491), though excellent for electrodeposited coatings, is not generally used for hot-dipped zinc coatings.

As with the German (1941) edition there is no index, and this is to be regretted. In a somewhat strangely worded preface the author explains that the detailed list of contents is better than an index. Many would

disagree and some would say that in a good scientific book both name and subject indexes are of great value. The references to the literature should also be brought into line with generally accepted practice.

The criticisms which have been made do not alter the fact that this is the only book in which so much information on various aspects of galvanizing has been collected together from various sources. Such a well-known and widely used book should be reliable and it is hoped that in the next edition more attention will be paid to this. The translation, although much better than in the last edition, still leaves room for improvement. Potential reversal is translated as " unpoling " and we have the usual " mixed crystal " for Mischkristall, although solid solution is also used ; " very gaseous " water is referred to on page 344, and martensite is described as " highly annealed " (p. 261).

The quality of the paper and the illustrations (with a few exceptions) are good. It is difficult, however, to justify the high price of 70/–. MARTIN L. HUGHES.

ELECTRON MICROSTRUCTURE OF STEEL

First Progress Report of Sub-Committee XI on Electron Microstructure of Steel to A.S.T.M. Committee E-4 on Metallography, reprinted from Proceedings of the American Society for Testing Materials, Philadelphia, Pa., U.S.A. pp. 49, heavy paper cover, $1.35.

THIS report, printed on good class paper to bring out details of the photomicrographs, was developed as a result of intensive work in Sub-Committee XI and will be of great interest to metallurgists and electron microscopists. Among other features it includes 47 specially prepared illustrations showing electron micrographs of various steel constituents.

The programme for the studies on which the report is based included variations in metallographic polishing and etching practices, replica techniques, and photographic procedures. Both mechanical polishing and electro-polishing were used to some extent, but mechanical polishing was used predominantly in obtaining the results reported. The etching reagents employed in this work were picral, nital, and ferric chloride-hydrochloric acid. Three replica techniques were investigated, namely, formvar, parlodion, and polystyrene-silica. Most of the formvar and parlodion replicas were shadow-cast either with chromium, platinum, or palladium to enhance the contrast. In general, the electron micrographs were made at an initial magnification of 5,000, and then were enlarged to a final magnification of 15,000. In addition to these high magnification micrographs, electron micrographs of these structures were prepared at an initial magnification of 750, and were enlarged to 2,500, in order to permit comparison with the light micrographs.

There can be no doubt that the inherent advantages of the electron microscope are of tremendous value in exploring the fine microstructures of steel, such as bainite, martensite, and tempered martensite, which are beyond the resolving power of the light microscope, and that it will assist considerably in advancing knowledge on the structure of metals.

Trade Publications

REFRACTORIES

AN excellent booklet has been published having for its object the explaining of the activities of Thomas Marshall & Co. (Loxley), Ltd., and its subsidiary and associated companies, with a view to extending the services the firm renders to users of refractories. No attempt is made to catalogue all its products, rather is a broad outline given of the firm's scope, such as might be gained from a visit to the works. In addition, however, the applications of the wide range of refractories manufactured are described. The history of Marshall's, from the crucible pot making days over a 100 years ago and the gradually increased services up to the present day, are briefly described. The scope of the parent Company to-day can be defined as being concerned with the manufacture of all type of refractories whose function is to assist in the pouring or casting of metals, and also with any field of usage that requires specialised shapes, using the widest interpretation of the description " fireclay " as the medium. The subsidiary and associated Companies extend this scope to cover the field of high-temperature insulation and the latest development of carbon as a refractory for blast-furnace linings and as a structural material where its chemical resisting properties commend it. This 76-page, $10\frac{1}{2} \times 8\frac{1}{2}$ in. booklet is exceedingly well produced and admirably illustrated, and users of refractories will find it not only interesting but very informative. Copies may be obtained free on application to Thomas Marshall & Co. (Loxley), Ltd., Storrs Bridge Works, Loxley, nr. Sheffield.

ENGINEERING PROPERTIES OF MONEL, NICKEL AND INCONEL

DESIGNERS and engineers will find all the essential data on Monel, Nickel and Inconel in this latest publication issued by Henry Wiggin & Co., Ltd. It is one of a series of data books presenting authoritative and comprehensive figures on physical and mechanical properties of the Wiggin high-nickel alloys. In addition to the usual tables of mechanical properties at normal temperatures, figures for high-temperature and low-temperature service are included.

Copies of this publication may be obtained free on application to: Henry Wiggin & Co., Ltd., Wiggin Street, Birmingham, 16.

MODERN MALLEABLE

UNDER the above title Hale & Hale (Tipton), Ltd. have published an informative booklet giving a brief description of the Hale foundries and their products. Beginning in a small way in 1909, this firm's forward policy, based on the highest possible quality of products and first-class service, has enabled it not only to erect modern factory buildings on a large scale but so to increase the demand for its products that extensions and improvements are continually in progress. This progress is due to the production and development of blackheart malleable castings, the production of which this firm has made a speciality. In addition, a special high-duty alloy, known as Permalite, has been developed, possessing mechanical properties in excess of standard blackheart malleable. Full information concerning the properties of these materials, the production of castings, treatment, machining, and reference is made to some applications. This 60-page, 9×7 in. booklet is bound in board covers, excellently arranged and printed, well illustrated, and contains very useful data and other information. Copies are available free on application to Hale & Hale (Tipton), Ltd., Dudley Port, Staffs.

LABORATORY METHODS
MECHANICAL · CHEMICAL · PHYSICAL · METALLOGRAPHIC
INSTRUMENTS AND MATERIALS
DECEMBER, 1950 Vol. XLII No. 254

A Test for the Dimensional Stability of Gauges by an X-ray Diffraction Method

By C. Wainwright, M.Sc., A.Inst.P.
and L. W. Nickols, B.Sc.(Eng.), A.M.I.Mech.E., A.M.I.Prod.E.
(Communication from the National Physical Laboratory)

Unless hardened steel gauges are given a low temperature stabilising treatment after hardening, a change in size amounting to as much as 0·0005 inch per inch may occur in the first twelve months of ageing. Hitherto, the only method of checking that the gauge has received the stabilising treatment has been by verifying that no change has occurred over a long period. To overcome the obvious disadvantages of this state of affairs, a method is described in which the breadth of the lines in the X-ray diffraction pattern of the steel are measured by the use of a Geiger-Müller counter spectrometer. The method will not, however, distinguish between the stable and unstable conditions if the gauge has been so severely heated in machining as to cause a structural change in the surface layers.

IT is customary to harden a high carbon tool steel blank intended for making into gauges or end-standards by quenching into cold water or brine from a temperature in the neighbourhood of 800° C., which is high enough to ensure adequate hardness but not so high that there is an appreciable risk of quenching cracks. It is well-known, however, that a steel which has been heat-treated in this way is not dimensionally stable, and if left on the shelf at normal temperatures undergoes changes in size which may amount to as much as 0·0005 inch/inch during the first twelve months of ageing. Instability of this order is naturally very undesirable, especially with end-standards, as their sizes are not known with certainty except at the actual time of measurement. Fortunately a stable condition is attained if a low temperature heat-treatment is given after quenching, and such a treatment is now a recommended practice. The procedure used in the Metrology Workshop of the National Physical Laboratory involves soaking for five hours at 150° C., followed by slow cooling in the furnace, and experience has shown that by this means a satisfactorily stable condition is produced without an undue reduction in hardness.

Basis of Method

Up to the present time the only practicable method of verifying that a steel gauge has actually received a stabilising treatment has been to make measurements of its size over a considerable period of time, and so to check that no alteration in size has occurred. There has not been readily available a satisfactory short-term testing process. On the other hand, the worker in the X-ray diffraction field has been aware that, as a laboratory technique, an examination of its X-ray diffraction spectrum is capable of giving information about the condition of a sample of steel. Over and above the production of a characteristic diffraction spectrum, normally recorded as diffraction lines upon a photographic film, these lines themselves vary in character with the condition of the steel. The X-ray lines from a hardened steel specimen are much broader and more diffuse (" martensite " lines) than those from the same specimen in the fully annealed condition (" ferrite " lines), and of intermediate breadth after partial annealing. Typical lines corresponding to the hardened and annealed conditions are shown in Fig. 1·

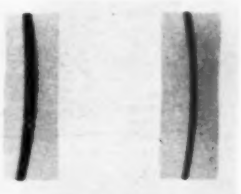


Fig. 1.—Showing the difference between X-ray line breadths obtained after hardening (left) and annealing (right) a high-carbon steel.

Thus, having established heat-treatment for a steel of a given composition, it is possible to develop the relationship between annealing temperature and line width and intensity, and to use the latter observations as a measure of the former. The process is, however, complicated and lengthy, as there is required not only the usual exposure, development, fixing, washing and drying of the film, but also a careful photometric survey across a selected X-ray line when the film is dry. In view of these disadvantages, there has been little reason for regarding the method as more than a laboratory process, to be applied on occasion to special problems.

These drawbacks are largely removed by the employment of the more recently developed Geiger-Müller counter X-ray technique, which replaces the photometric observations from photographic film by the direct counting or recording of X-ray intensity in terms of electrical pulses, their production rate being proportional to the intensity of the X-rays entering the counter tube through a narrow slit. By the use of a Geiger-Müller

counter attached to an X-ray spectrometer, the intensity of an X-ray diffraction line may be measured at different places across its breadth and a graph of the intensity plotted on a base corresponding to the line width. This simplified procedure has been applied to the problem of dimensional stability.

A single specimen of a gauge steel was heat-treated to bring it successively into the hardened, the hardened and stabilised, and the fully softened conditions, a Geiger-Müller counter survey of the strongest (110) X-ray line being made at each stage. The three line shapes are shown in Fig. 2. These curves illustrate the anticipated large difference between the line shapes obtained for the extreme conditions, but for the immediate purpose it is more significant that a sufficient difference exists between the curves for the as-quenched and the stabilised material. Each curve was surveyed and plotted in a period of about thirty minutes.

Practical Considerations

At this stage it was necessary to consider the practical circumstances governing the testing of a gauge by the X-ray method. It is known that dimensional instability is not the direct result of internal stresses set up in the material during the hardening process but is connected with slow modifications of the metallurgical structure of the steel, the dimensional changes being dependent on the mass as a whole. The X-ray diffraction examination is essentially a surface test, the penetration being of the order of 0·0005 in. If the evidence provided by the method is to be adequate, it follows that the results obtained from the surface layers must be directly related also to the mass of the specimen, or a definite correlation must exist between surface and internal conditions. In the case of hardened gauges the criterion will normally be satisfied, for if the specimens are small they will be hardened throughout, and if large, the interior will be softer and less likely to display instability than the outer regions. A surface observation should in both cases provide a definite indication of the tendency towards instability. The whole of this correlation is destroyed if the finishing processes which follow the heat treatment create new conditions in the surface layers so that the observations from them are no longer related to the previous heat treatment or to the internal condition.

In general the possibility of newly heat treated samples having decarburised surface layers cannot be neglected,

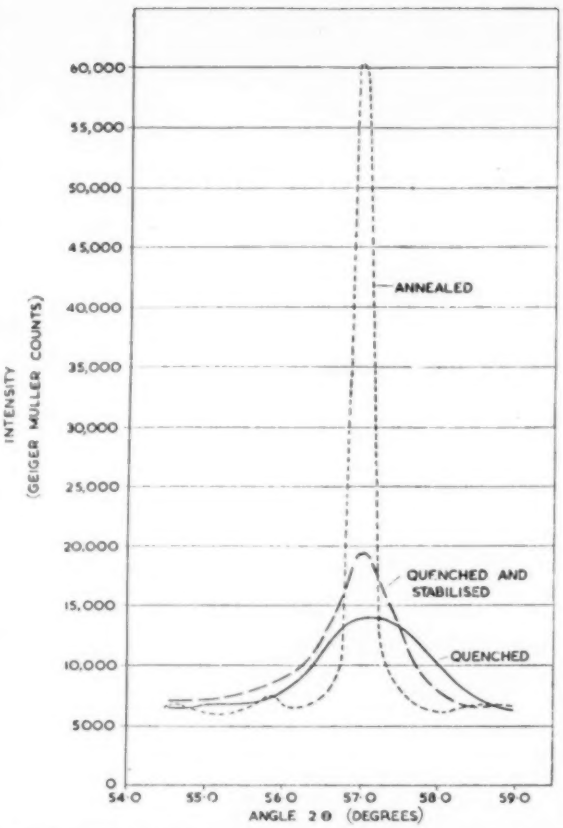


Fig. 2.—Effect of various heat treatments on the shape of (110) X-ray diffraction " line " from a 1·3% C. steel.

but finished gauges have had these outer layers removed during the subsequent machining processes.

Gauge surfaces are of two kinds. Whereas gauging faces have undergone fine grinding and possibly lapping during the later stages of their preparation, non-gauging surfaces, if they have been worked at all, have probably received a rougher treatment. Consideration of such aspects made it evident that the successful application of

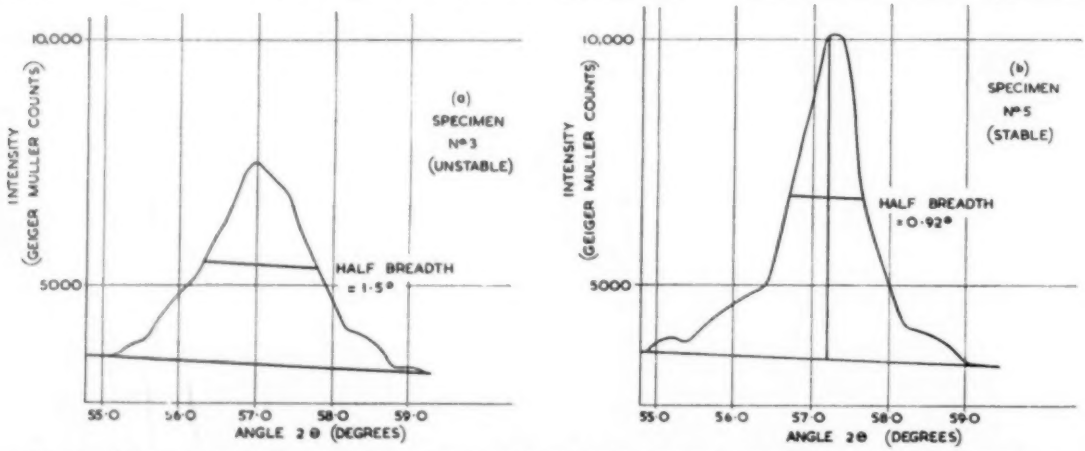


Fig. 3.—Shapes of (110) X-ray diffraction " line " from a hardened and unstabilised, and a hardened and stabilised steel.

F = Fine ground—fine cuts (2 × 0·0003 in.)
G = Fine ground—fine cut (1 × 0·0005 in.)
H = Fine ground—heavy cut (1 × 0·003 in.)
L = Lapped (0·0002 in.)
P = Polished (0·002 in.)
Q = Quenched
R = Rough ground—heavy cuts (2 × 0·003 in.)
S = Quenched and stabilised

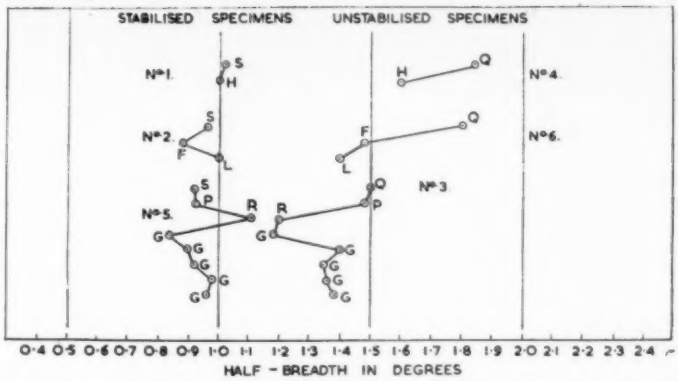


Fig. 4.—Effect of finishing process on half-breadths of (110) X-ray diffraction " line " from a 1·3% C. steel.

an X-ray diffraction examination to gauges after the commencement of the final working operations would depend on the steel in the surface layers remaining unaffected. Further experiments were therefore devised to test the effect of working processes, i.e., fine and rough grinding, lapping and polishing, on the surface layers of a gauge steel in the stable and unstable forms.

Six cylindrical blocks of 1·3% C tool steel, each 0·5 in. diameter by 0·5 in. long, were hardened by quenching from a cyanide bath at 780° C., three of them subsequently receiving the stabilising treatment of 5 hours at 150° C. All the specimens were then examined on the Geiger-Müller counter spectrometer, the only preparation being the removal of a vestige of scale by hydrogen attack in an electrolytic sodium cyanide bath. One end of each specimen was used for the X-ray examination. Fig. 3 (*a*, *b*) shows typical curves from the unstable and stable specimens. The second end-face of each specimen was ground flat to serve as a reference surface for measuring the amounts of metal removed by the later processes.

The criterion of the shape of a curve was its half-breadth, that is the breadth measured half-way between peak and background levels. From considerations of geometrical similarity this measurement is independent of overall intensities, so long as working conditions remain steady during the time required for any one survey. When half-breadths were measured in this way, it was found that the three values from the stabilised specimens were between 0·9° and 1·0°, this range being approximately the same as the anticipated experimental error, and those from the as-quenched specimens were 1·5°, 1·8° and 1·8°. The reason for the rather wide range in the second case was not investigated, for in view of the general tendency for later results from unstable material to be grouped between 1·4° and 1·5°, the lower figure of 1·4° was chosen as the criterion, the essential feature being that the interval between this minimum value and the upper limit of the results from the stable material was sufficiently large compared with experimental error.

The specimens were next grouped into pairs, each consisting of a stable and an unstable specimen, and each pair was subjected to one or more of the following working operations, which were carried out according to regular practice and without special instructions of any kind.

1. Rub down through successive grades of emery paper to 00 grade.
2. " Fine finish " ground (dry)—2 × 0·0003 in. fine cuts.
3. " Fine finish" ground (dry)—1 × 0·003 in. heavy cut.
4. After (2)—lapped.
5. Rough ground (dry)—2 × 0·003 in. heavy cuts.
6. After (5)—removal of surface by five successive " fine finish " cuts (dry) of 0·0005 in. each, making 0·0025 in. in all.

The subsequent half-breadth measurements are displayed in Fig. 4.

None of the primary operations 1–4 caused any significant modifications of the surface conditions and

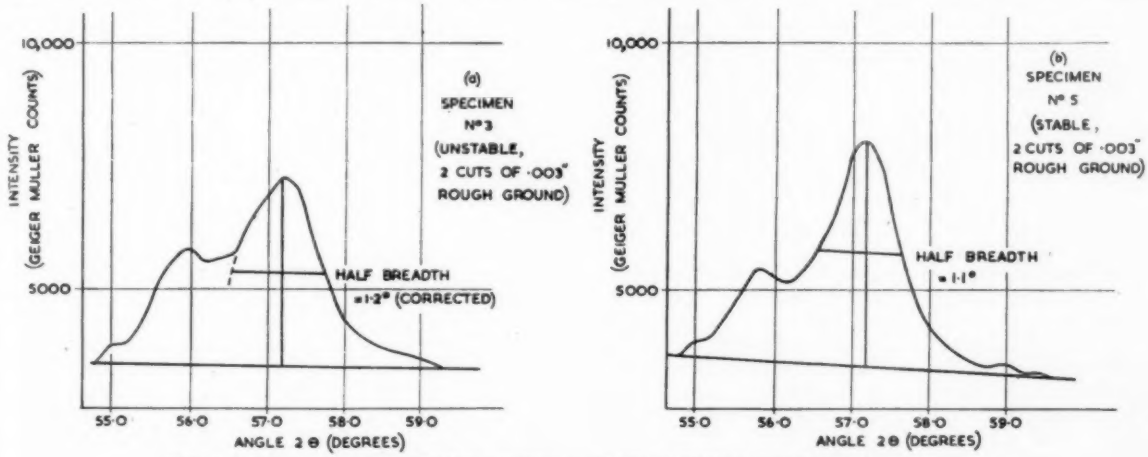

10,000
5000
INTENSITY (GEIGER MÜLLER COUNTS)
(a)
SPECIMEN N°3 (UNSTABLE, 2 CUTS OF ·003" ROUGH GROUND)
HALF BREADTH = 1·2° (CORRECTED)
55·0 56·0 57·0 58·0 59·0
ANGLE 2θ (DEGREES)
(b)
SPECIMEN N° 5 (STABLE, 2 CUTS OF ·003" ROUGH GROUND)
HALF BREADTH = 1·1°

Fig. 5.—Effect of rough grinding process on shape of (110) X-ray diffraction " line."

the corresponding curves are represented satisfactorily by those of Fig. 3. Like the original values, the plotted half-breadths of Fig. 4 lie between 0·9° and 1·0°, and above 1·4°, for the stable and unstable specimens respectively.

On the other hand the curves of Fig. 5 (*a*, *b*) show very clearly that the rough grinding process caused a marked alteration in the surface layers. In each case there was a significant modification in the form of a second peak corresponding to the presence of a substantial amount of the high temperature phase, austenite, in the surface layers. Also, when the half-breadths of the martensite lines were measured (a simple construction being used in Fig. 5 (*a*)), they were found to lie close together with values intermediate between those for the stabilised and unstablised conditions. It was evident that as the grinding wheel passed over the faces of the specimens, each elementary area was in turn raised momentarily to a high temperature within the austenitic range and then cooled by conduction of heat to the interior in such a way that a proportion of the austenite remained untransformed. The closeness of the half-breadth values showed that to the depth of penetration of the X-rays the final condition of the martensite content was in both cases the consequence of the rough grinding, and that correlation with the original conditions had disappeared.

In order to determine the depth of these modifications, successive 0·0005 in. thick layers were removed from both specimens by fine-finish grinding, an X-ray survey being made at each stage. The removal of 0·001 in. (two cuts) proved to be sufficient to restore the half-breadths to their original values, while only a vestige of austenite remained after four cuts.

Conclusions

The above experiments have made it possible to establish a number of conclusions—

(1) By means of an X-ray diffraction examination it is possible to distinguish between samples of gauge steel which have been quenched from 780° C., and those which in addition, whilst being otherwise similar, have received the stabilising heat-treatment of 5 hours at 150° C. The criterion used is the shape of the X-ray lines obtained from the steel in the two conditions, and in particular a quantitative measurement of the breadth of the lines.

By making use of the Geiger-Müller counter X-ray diffraction technique the observations may be obtained by a simple and direct measuring operation with a reasonable time schedule.

The limited X-ray diffraction examination described above will not, however, necessarily distinguish between two samples of the same composition, which have received a low temperature heat treatment following quenching, but with somewhat different conditions of temperature and time, one gauge being rendered stable and the other almost stable.

(2) The surface conditions are not affected by subsequent dry fine grinding or lapping operations. If any modification of the surface layers occurs the effective depth is small compared with the depth of penetration of the X-rays.

(3) Dry rough grinding causes a modification of the surface conditions due to a momentary over-heating of the extreme surface layers, followed by an immediate quenching due to loss of heat to the interior. Thus a quantity of retained austenite is to be found at the surface, and half-breadth values no longer give an indication of the previous heat-treatments. These untoward effects may be removed by further "fine-finish" grinding. With the particular rough grinding treatment of this investigation they were found to persist to a depth of about 0·002 in.

(4) The work has been directed primarily to discovering whether gauging surfaces of finished gauges may be used for the purpose of X-ray diffraction tests for dimensional stability. The method would also appear to be applicable to the testing of blanks from workshop production, e.g. as sampling tests, immediately after heat-treatment and before any of the normal finishing operations have commenced, this procedure corresponding to the examination of the specimens of the present experiments in their initial heat-treated condition. For such applications it would be necessary to ensure that the heat-treated surfaces have not suffered any deleterious modifications, e.g., decarburisation, or if this has occurred, to remove sufficient material from the surfaces by one of the admissible processes before making the X-ray test.

It must be emphasised that the half-breadths of the X-ray lines are dependent on the quenching temperature and on the composition of the steel, and are also directly affected by experimental criteria such as the width of the X-ray beam and the size of the Geiger-Müller counter tube aperture. Thus the values now obtained are to be regarded as significant for the purpose of comparison but not as measures of absolute half-breadths.

During the course of this work the roughness of the various surfaces produced by the grinding and other operations was measured by means of a Talysurf. Rough ground surfaces were found to have surface roughness values of 55–60 micro-inches average index value, fine ground surfaces to have values of 4–12 micro-inches, and lapped or hand polished surfaces to have values of 1 micro-inch or less.

Acknowledgments

The problem was suggested by Mr. F. H. Rolt of the Metrology Division of the National Physical Laboratory and his interest and help in arranging the tests of the stability of the gauges are acknowledged. The work was carried out as part of the research programme of the National Physical Laboratory, and this paper is published by permission of the Director.

High Speed Copying Developer

INCREASING use of document copying machines has created a demand for a developer functioning within the range 30–60 seconds normally allowed for in the time cycle on which document copying machines operate. 'Planocop' document copying developer has been specially formulated to give images of good contrast and density with an exceptionally low fog level. The developing time can be fixed at any point between 20 and 120 seconds by suitable adjustment of the dilution.

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May & Baker, Ltd., Dagenham.

Determination of Silicon, Copper and Iron in Silicon Bronze Hardeners

By George Norwitz and Irwin Norwitz*

THERE is nothing in the literature concerning the analysis of silicon bronze hardeners, although this type of material is frequently used in the manufacture of silicon bronzes[1]. Silicon bronze hardeners are a unique copper-base alloy in that they contain copper silicides, iron silicides and elemental silicon, none of which are attacked by fuming with perchloric or sulphuric acid. The determination of silicon, copper and iron, therefore, presents a problem, especially since it is not possible to dissolve a copper-base alloy by heating with sodium hydroxide solution, or by fusing with sodium carbonate or sodium peroxide.

The authors conducted an investigation into the analysis of silicon bronze hardeners and developed rapid, accurate methods for the determination of silicon, copper and iron. In the determination of the silicon the sample is dissolved with nitric acid, perchloric acid is added and the solution evaporated to fumes with perchloric acid. The solution is filtered, the filter paper burned off, and the residue fused with sodium carbonate. The silicon is then dehydrated with perchloric acid in the normal manner. For the determination of copper and iron the sample is dissolved in a mixture of nitric and hydrofluoric acid, perchloric is added and the solution is evaporated to fumes of perchloric acid. The copper is then electrolysed from a perchloric-nitric acid medium. The electrolyte is evaporated to fumes of perchloric acid, hydrochloric acid is added, the iron reduced with stannous chloride and titrated with permanganate. The other elements which may be determined in the analysis of brasses and bronzes are present in silicon bronze hardeners only in residual amounts. If their determination is required the A.S.T.M. methods for silicon bronze[2] can be used.

Special Reagents

Stannous Chloride Solution (15%).—Dissolve 150 grams of $SnCl_2 . 5H_2O$ in 300 ml. of hydrochloric acid and dilute to 1 litre with water.

Titration Mixture.—Dissolve 200 grams of $MnSO_4 . 4H_2O$ in 1 litre of water and add a cooled mixture of 400 ml. of sulphuric acid, 1,200 ml. of water and 400 ml. of phosphoric acid (85%).

Procedure

Determination of Silicon.—Add 15 ml. of nitric acid (1 to 1) to a 0·5 gram sample contained in a 400-ml. beaker and warm on the hot plate for a few minutes. Add 30 ml. of perchloric acid (70%), evaporate to fumes of perchloric acid and reflux for 20 minutes. Cool, add 100 ml. of water and filter through a No. 41H Whatman filter paper. Swab and wash with water. Transfer the filter paper and precipitate to a platinum crucible, and burn off the filter paper by heating in an open muffle at dull red heat. Cool. Fuse with 10 grams of sodium carbonate, and transfer the crucible and melt to the original 400-ml. beaker. Add 100 ml. of water and 30 ml. of perchloric acid (70%) and warm on the hot plate until the melt is dissolved. Remove the crucible. Evaporate to fumes of perchloric acid and reflux for 20 minutes. Cool, add 100 ml. of water, and filter through a No. 41H Whatman filter. Swab and wash with water. Transfer the filter paper and precipitate to a platinum crucible and burn off the filter paper by heating in an open muffle at dull red heat. Ignite at 1,100° C. for 30 minutes, cool, and weigh. Add 2 drops of sulphuric acid (1 to 1) and 5 ml. of hydrofluoric acid, and evaporate to dryness by heating on the steam bath. Evaporate off the sulphuric acid by heating on the hot plate. Ignite at red heat for 10 minutes, cool and weigh, the difference in weight is SiO_2. The factor for converting SiO_2 to Si is 0·4672.

TABLE I.—RESULTS FOR SILICON, COPPER AND IRON IN A TYPICAL SILICON BRONZE HARDENER.

Silicon %	Copper %	Iron %	Total* %
21·19	70·95	7·80	99·94
21·10	70·90	7·85	99·85
21·12	70·91	7·86	99·89

* Nickel, manganese, tin, lead and aluminium were present in the sample in residual amounts only.

Copper and Iron.—Add 30 ml. of nitric acid (1 to 1) to a 1 gram sample contained in a 300-ml. electrolytic beaker and warm on the hot plate for a few minutes. Add a few drops of hydrofluoric acid to dissolve the silicon. Add 12 ml. of perchloric acid (70%) and evaporate to fumes of perchloric acid. Cool. Dilute to 190 ml. with water and add 7 ml. of nitric acid. Electrolyse with stirring for 90 minutes at 2 amp/sq. dm., using platinum gauze cathodes and platinum spiral anodes. With the current on, drop the beaker containing the electrolyte while washing the electrodes with a stream of water. Immerse the cathodes in water and then in alcohol, dry at 110° C. for 3 minutes, cool, and weigh the deposit as metallic copper. Evaporate the electrolyte from the copper determination to strong fumes of perchloric acid. Cool. Add 20 ml. of water and 5 ml. of hydrochloric acid, and heat to about 80° C. Add stannous chloride solution (15%) dropwise with stirring until the solution becomes colourless, and then add one drop in excess. Wash down the sides of the beaker and cool the solution in ice-water. Add at one stroke 10 ml. of saturated solution of mercuric chloride and allow the solution to stand in the ice-water for 2 to 5 minutes. Wash the solution into a 600-ml. beaker containing 400 ml. of cold water and 25 ml. of titration mixture. Titrate with 0·1 N potassium permanganate solution until a definite pink colour is obtained. Deduct a blank, and calculate the percentage of iron. The potassium permanganate is standardised against sodium oxalate.

Results

The results obtained when a representative silicon bronze hardener was analysed three times by the proposed procedure are shown in Table I. The results show the precision of the methods rather than their accuracy. Since no standard sample for this type of material is obtainable, and since the preparation of a synthetic sample is not possible, the usual methods for checking accuracy cannot be employed. However, the fact that the total of silicon, copper and iron is close to 100% indicates that the method has satisfactory accuracy.

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1 Crown, J. E. *Foundry*, 70, No. 8, 65 (1942).

2 American Society for Testing Materials, "A.S.T.M. Methods of Chemical Analysis of Metals," p. 197, Philadelphia, Pa. 1946.

Bureau of Analysed Samples, Ltd.

BEFORE the war it was customary for the Bureau of Analysed Samples, Ltd., which is responsible for the supply of British Chemical Standards, to hold general meetings of co-operating chemists at intervals of three years. As a result of the conditions prevailing during and since the war, a period of twelve years elapsed between the last pre-war meeting, held in 1938, and that held at the Station Hotel, York, on November 28th, 1950.

Following a welcome by the Chairman, Dr. E. Gregory, details of changes in the Honorary Advisory Committee were announced. The present members are: B. Bagshawe, Brown-Firth Research Laboratories; T. Dennison, B.I.S.R.A.; F. H. Edwards, Bragg Laboratory; P. Good, B.S.I.; T. G. Pearson, British Aluminium., Co. Ltd.; G.E. Speight, United Steel Co. Ltd.; and W. Westwood, B.C.I.R.A.

For the benefit of those attending for the first time, Mr. N. D. Ridsdale, Managing Director, gave a brief account of the early history of the movement prior to presenting his report on the progress made in the preparation, use, and analytical accuracy of British Chemical Standards. Since 1938, the number of Standards available has increased from 41 (representing some 200 standardised elements or constituents) to 68 (representing 350 or so constituents). Included in the present list are eight pure metals or reagents and eight spectrographic standards. Special methods are used to get fine machinings and precautions are taken to remove moisture, and in some cases oxygen, during storage.

The use of the Standards for checking routine analyses and new methods of analysis are well known and more recently they have been adopted for the preparation of graphs for photometric methods, using a series with progressive increments of different elements. They are particularly valuable in cases such as silicon where the preparation of a standard soluble silicate solution is not very simple. The combustion sulphur and spectrographic methods are completely dependent on chemical standards.

It is difficult to assess precisely how many disputes on analysis have been avoided or settled by the use of B.C.S., but there must have been a large number. Perhaps the most important contribution these standards have made in their own field is that they have brought chemists all over the country into more intimate and friendly contact with each other, given them a much better knowledge of the standard of accuracy of their own work and of the methods they have been using and, most important of all, promoted a great deal of goodwill.

In reporting on the demand for B.C.S. at home and overseas, Mr. P. D. Ridsdale disclosed that sales had increased from some 400,000 g., in the three years 1936–38, to over 1,250,000 g. in 1947–49, mainly as a result of increased demand for existing standards. Although the chief demand is still for carbon steels, standards for alloy steels, cast irons, ferro-alloys and non-ferrous metals form a greater percentage of the total sales than they did in 1938. Demand for the recently introduced spectrographic standards is promising and 40 sets have already been sold. The sales of the special student samples have considerably increased, the total for the past three years amounting to 250,000 g. Some 20% of all standards have been exported in the last three years.

Both speakers paid tribute to the work of the co-operating chemists, without which it would not have been possible to meet the increased demand by renewing existing standards and preparing new ones. In the ensuing discussion, numerous suggestions were made for the provision of new standards. These included: a standard basic slag for use in the sulphur partition method of controlling the operation of basic open-hearth furnaces; zinc-base alloys; an impure 'pure copper'; a complex aluminium bronze; an 85–5–5–5 gunmetal; a Pb–Sn–Ag–Sb type solder; an aluminium—7% magnesium alloy (D.T.D. 300); an aluminium—3–6% magnesium alloy; a nickel silver; a lead-free copper-base alloy with 1·0% Fe, 0·75% Mn and 0·75% Ni, as a spectrographic standard; a 'pure aluminium' with 1% Fe, 0·5% Mn, 0·75% Ni, 0·5% Si, 1% Cu and 0·1% Ti; a steel containing nitrogen; steels with 0–0·1% Al, as a spectrographic standard; and an 18 : 8 stainless steel of low carbon (0·03%) with low copper.

Meters and Instruments for the Efficient Use of Fuel

AT the Fuel Efficiency Exhibition which was held at City Hall, Manchester, from November 22nd to December 2nd, 1950, George Kent, Ltd., exhibited an extremely comprehensive range of meters and instruments for efficient use of fuel in industry. They comprised the mechanical and differential boiler feed meters, Brodie-Kent positive displacement meters for petrol, oil, and other petroleum products, integrating and recording steam flow and oil meters, combustion efficiency meters, ring balance meters for low pressure air and gas measurement fitted with Mark 20 Air Operated Control and operating a power cylinder connected to a model butterfly valve. Also the range of Multelec potentiometric instruments for measurement and control.

To raise steam without using too much fuel, the best evaporation conditions are required, coupled with the best combustion. In large power plants, these results are obtained by the use of carefully selected instruments mounted on panels of individual design. By standardising the "Stoker's Mate," George Kent, Ltd., now make available for the small steam raising plant a combination of standard Kent instruments identical in quality and performance to those which they supply for larger plants. This equipment includes a feed-water meter (Kent RW/C) and a KM meter for recording steam flow, with a counter giving the total steam passed. To check combustion, a Kent Multelec is used.

Lecture Courses in Process Instrumentation

COURSES in this subject have recently been initiated by the Department of Coal, Gas and Fuel Industries with Metallurgy at the University of Leeds. The course, which will ultimately be taken by all degree and post-graduate diploma students in the subjects of gas and chemical engineering, ceramics and process metallurgy, is to be given in two parts. The first part, which has commenced in the current session, is "The Measurement of Process Variables" and deals with principles and methods of measuring such quantities as pressure, temperature, fluid flow, etc. The second part "Automatic Control" will commence in the following session and will deal with the theory and practice of automatic controls as applied to the process industries. These lecture courses are open to external students by arrangements with the Department of Extra-Mural Studies.

Some New Indicators in Various Titrimetric Processes

By A. J. Nutten, B.Sc., A.R.I.C.

Department of Chemistry, The University, Birmingham

New acid-base, redox and iodometric indicators were discussed in the September and October issues. In this concluding article the author considers bromometric (reversible and irreversible) indicators, absorption indicators and miscellaneous indicators.

IV.

BROMOMETRIC INDICATORS

(a) IRREVERSIBLE TYPE

For many years the presence of free bromine has been detected by methyl orange, methyl red, and indigo-carmine. The colour of these indicators is destroyed by bromine, but the colour change is not reversible, since the indicators themselves are decomposed.

New indicators for use in bromate titrations have been described by Smith and Bliss.[55] They are :

Chrysöidine (British Colour Index No. 21)

Bordeaux (British Colour Index No. 88)

Naphthol Blue Black (British Colour Index No. 246)

Indicator Solutions : A 0·1% solution of the dyestuff in distilled water. A few drops/100 ml. solution.

Smith and May[56] used Bordeaux, Naphthol Blue Black, and

Brilliant Ponceau 5R

(British Colour Index No. 185)

(0·2% aqueous solution) for the titration of As^{+3} and Sb^{+3} in hydrochloric acid solution at room temperature. The intense colour of the dyestuffs permits the use of 0·1–0·2 ml. of a 0·1–0·2% solution for titration. The potentials at which they are oxidised and the colour destroyed, using hydrochloric acid solutions of bromate as oxidant, are above the equivalent point potential for the oxidation of As^{+3} and Sb^{+3} to the pentavalent state.

The indicators are irreversible, decolorisation of the solution signifying the end-point. To avoid the danger of mistaking the end-point a few drops of fresh indicator are added at, or near, the end of the reaction.

Results obtained using solutions of different acid concentrations were all within 0·15% of theory. The procedure is superior to the older Györy method in that it does not require titration either in the hot, or at higher acid concentrations.

Fluorescein

Hahn[57] has used fluorescein as an irreversible indicator in the bromometric titration of arsenious acid.

Indicator Solution : 0·1 g. fluorescein dissolved in 100 ml. of distilled water containing a few drops of sodium hydroxide solution. 1 drop/10 ml. solution.

At the end-point the greenish-yellow colour of the solution changes to a reddish-brown. The colour transition is slow but heating the solution to 40°–50° C. accelerates the reaction.

(b) REVERSIBLE TYPE

Although there is an obvious need for reversible bromate indicators, little attention has been directed this need.

Irreversible indicators suffer from the disadvantage that local excesses of bromine may bleach the indicator before the end-point is reached, necessitating slow addition of bromate.

A number of new indicators have been discovered during the last 15 years but these appear to have received little attention. Belcher[58] has recently reviewed those now available and has carried out a critical examination of the more promising ones.

He found that α–naphthoflavone, p–ethoxychrysöidine, and fuschin were satisfactory for titrations of As^{+3}, but that α–naphthoflavone was superior to the others. He did not examine the application of these indicators to Sb^{+3} titrations. Later, however, he reported[54] that α–naphthoflavone was not as satisfactory as p–ethoxy-chrysöidine for Sb^{+3} titrations, as at least double the usual amount of indicator is necessary, and the end-point is not so sharp. He suggested that the tartrate ion, necessarily present to prevent hydrolysis, was probably responsible. p–Ethoxychrysöidine appears to be unaffected under these conditions.

α–Naphthoflavone

$$\text{Pale–Yellow} \xrightarrow{Br_2} \text{Orange–Brown}$$

Gotô[59] first showed that α-naphthoflavone could be used as a reversible indicator for bromate titrations.

Indicator Solution : A 0·1% solution of α–naphtho-flavone in ethanol or glacial acetic acid.

On addition of the indicator to the solution to be titrated, a colloidal solution is formed. Excess bromine changes the indicator from a pale-yellow to a deep orange-brown, the colour change taking place on the surface of the colloid. Addition of excess arsenite restores the original pale-yellow colour.

As an indicator in titrations involving iodine, α-naphthoflavone is 5 times more sensitive than starch indicator.

p–Ethoxychrysöidine

$$\text{Red} \xrightarrow{Br_2} \text{Orange–Yellow}$$

p–Ethoxychrysöidine is an excellent multiform indicator, having being used in acidimetry, alkalimetry, argentometry and bromometry by Schulek and Rósza[60]. Belcher[54] has used it in iodate titrations, while it has also been used as an indicator in the titration of zinc with potassium ferrocyanide.

A solution of potassium bromide in sulphuric acid becomes red on addition of the indicator. The red colour deepens on addition of a drop of dilute potassium bromate solution, but further addition of the oxidising agent bleaches the solution to an orange-yellow colour. On addition of excess arsenite to the bleached solution the indicator reverts to its red colour. The end-point, however, is never as sharp as the original

change, and Belcher[54] suggests that this may be due to a certain amount of destruction of the indicator.

Indicator Solution : A 0·05–0·1% solution of p–ethoxychrysöidine in ethanol.

V. ADSORPTION INDICATORS

Bromothymol Blue

Colourless —→ Blue

Mehrotra[61] has described the applicability of bromothymol blue to the argentometric titration of thiocyanate ions.

Indicator Solution : A 0·1% solution of bromothymol blue in ethanol.

Two drops of indicator are added to 10 ml. 0·1 N thiocyanate solution and 0·1 N silver nitrate run in. Each drop of silver nitrate produces a blue colour where it comes in contact with the suspension, and at the end-point ½ drop of silver solution turns the precipitate blue. The colour change is sharp and reversible though not well-defined for solutions about 0·01 N. Titration is not possible at a *p*H less than 7.

Coagulation of the silver thiocyanate begins quite early, but the precipitate and supernatant suspension remain colourless as long as thiocyanate ions are in excess.

Bromocresol Purple

Indicator Change : Violet —→ Colourless

Precipitate Change : Colourless —→ Bluish-Green

Bromocresol purple[61] is used in the same way as bromothymol blue in the titration of thiocyanate ions with silver solution.

Indicator Solution : A 0·1% solution of bromocresol purple in ethanol.

The precipitate remains colourless and the supernatant suspension violet while the thiocyanate is present in excess. At the end-point, the suspension becomes colourless and a bluish-green colour develops simultaneously on the particles of the coagulated precipitate. The end-point is stated to be sharper than that obtained with bromothymol blue. The titrations can be carried out in 0·01 N solutions, though not at a *p*H less than 7.

Bromophenol Blue

Colourless —→ Blue (CNS^- by Ag^+)

Greenish-Yellow —→ Green (Tl^+ by I^-)

According to Mehrotra,[61] bromophenol blue can be used as an adsorption indicator in the same way as bromothymol blue, though in this case the solution to be titrated may be at a *p*H as low as 3 and at a concentration of 0·004 N. In the acidic solutions, the supernatant liquid remains colourless if thiocyanate ions are in excess and becomes blue at the equivalence point.

Bromophenol blue may also be used as an adsorption indicator in the volumetric determination of thallium[62].

Indicator Solution : A 0·1% solution of bromophenol blue in 80% ethanol. 3–4 drops per titration.

Procedure : Place 20 ml. 0·1 N potassium iodide (previously standardised) in a beaker, add 3–4 drops indicator and titrate with 0·1 N thallous nitrate or sulphate. Reddish-yellow thallous iodide begins to coagulate when about 15 ml. titrant have been added, the supernatant suspension remaining violet in colour. A few drops before the end-point, the coagulating particles begin to lighten in colour, whereupon the titration should be continued carefully and with shaking after addition of each drop of the thallous solution. At the end-point, the greenish-yellow precipitate changes to rich-green in colour. The titration should preferably be carried out in diffuse light and the indicator added near the end-point.

Lead interferes but may be removed by adding a slight excess of potassium sulphate. No interference occurs, however, if titration is effected with thallous sulphate, provided that lead ions are present in amounts less than equivalent to the amount of potassium iodide taken.

Chromate and thiocyanate interfere.

The end-point is sharp at *p*H 4–8 and when the titrating solutions have a concentration of 0·2 N to 0·04 N.

Four adsorption indicators for the titration of silver with thiocyanate have been proposed by Uzumasa and Miyake.[63] The indicators are used in a slightly alkaline condition :

Sodium Alizarin Sulphonate

Yellow —→ Pink

Minimum effective concentration of medium — 0.033 N

Phenolphthalein

Pink —→ Purple

Minimum effective concentration of medium — 0.01 N

Cochineal

Purple —→ Green

Minimum effective concentration of medium — 0.01 N

Phenol Red

Red —→ Violet

Minimum effective concentration of medium — 0.01 N

Congo Red

Blue —→ Red

Congo Red[64] as an adsorption indicator in halide and thiocyanate determinations possesses both acidic and basic properties, and can be adsorbed by both positively and negatively charged particles.

The colour change is particularly sharp (blue to red), addition of dextrin rendering it even sharper. It is readily reversible and titration may be effected from either direction. The best *p*H range for the titration is 3–5.

Resorcinol-Succinein

Mehrotra and co-workers[65] used resorcinol-succinein as an adsorption indicator in argentometry.

Indicator Solution : A 0·2% solution of resorcinol-succinein in ethanol. 2 drops/20 ml. solution.

The titration fails in acid solutions, but is possible in neutral or slightly alkaline solutions.

Mercurochrome

Colourless —→ Pink

Mercurochrome is generally used as an acid-base indicator, but Airan and Ghatage[66] have used it successfully as an indicator in halogen and silver ion titrations.

Indicator Solution : A 0·1% solution of mercurochrome in distilled water. 2–3 drops per titration.

Procedure : To 10 ml. halide solution (containing 1·5 ml. concentrated sulphuric acid and 1·5 ml. phosphoric acid) add 2–3 drops indicator, and titrate with 0·05 N silver nitrate to a persistent pink colour.

The above workers give no results but claim satisfactory agreement with results obtained using alkali chromate as indicator.

Tartrazine

Berry and Durrant[67] used tartrazine as an adsorption indicator in the titration of silver with bromide. The precipitate first adsorbs the dye and remains yellow as long as silver ions are present in excess. At the end-point the tartrazine is displaced and produces a greenish-yellow colour in the liquid. The first visible green colour appears 0·2–0·25% before the end-point, but an accuracy of 0·1% may be achieved by titration to a deeper green.

In a later paper Berry[68] describes the use of tartrazine as indicator in the Volhard determination of chloride.

Indicator Solution : A 0·5% solution of tartrazine in distilled water. 3 drops per titration.

The main feature of its use in this connection is that titration can be effected without filtration or protection of the precipitate by nitrobenzene. In his titration experiments, Berry added weighed quantities of silver nitrate to the same volume of approximately 0·1 N hydrochloric acid and completed the titration either with the same hydrochloric acid or with a solution of ammonium thiocyanate.

For the determination of chloride solutions, excess silver nitrate solution is added and the excess silver determined with either hydrochloric acid or ammonium thiocyanate (one would expect in the latter case metathesis between the slightly soluble silver chloride and the ammonium thiocyanate). The end-point is indicated when the dye is removed from the precipitate and the supernatant liquid assumes a rich lemon colour.

VI. MISCELLANEOUS INDICATORS

Nickel Dimethylglyoxime

Colourless ⟶ Pink

When a solution of silver nitrate is added to a cyanide solution the complex argentocyanide ion is formed :

$$Ag^+ + 2\ CN^- \rightleftharpoons Ag\ (CN)_2^-$$

Ubbelohde[69] proposed nickel dimethylglyoxime as indicator for the determination of cyanide.

Indicator Solution : To a 5% potassium cyanide solution add an equal volume of ethanol and boil with an excess of solid nickel dimethylglyoxime. Cool, filter, and dilute the solution with 10 times its volume of water. A colourless solution results. A few drops per titration.

The titration of the cyanide solution is carried out with silver nitrate. As long as the cyanide ion is present in excess, the nickel in the indicator remains bound as the colourless cyanonickel dimethylglyoxime complex. When, however, the cyanide is no longer in excess, silver ions combine with the cyanide of the indicator complex (see equation above) and the characteristic pink colour of nickel dimethylglyoxime appears.

It is essential that the titration be carried out slowly and with thorough shaking near the end-point. Good colour changes have been obtained in 0·1 N solutions.

p-Dimethylaminobenzylidene Rhodanine

Colourless ⟶ Red-Violet

The end-point in the titration of cyanide with silver nitrate may also be detected with p-dimethylaminobenzylidene rhodanine.[70]

Indicator Solution : A 0·02% solution of p-dimethylaminobenzylidene rhodanine in acetone. 3 drops per titration.

When the silver ion is in excess, the red coloured silver complex of the indicator is formed. Other heavy metal ions must be absent.

Procedure : Add 10 ml. 10% sodium hydroxide solution and 3 drops indicator to the cyanide solution. Titrate with 0·1 N silver nitrate to the first appearance of a red colour. The end-point is very sharp in dilute solutions (0·02 N or less).

o-Dianisidine

Red-Brown ⟶ Pale-Green

It has long been known that zinc may be determined titrimetrically by precipitation with potassium ferrocyanide. Several indicators have been recommended for the detection of the end-point, the most promising being o-dianisidine.[71]

Potassium ferrocyanide normally contains a trace of ferricyanide which gives a red colour with o-dianisidine in acid solution. At the end-point of the titration, a drop of ferrocyanide in excess lowers the oxidation potential sufficiently to discharge the red colour. The o-dianisidine functions, therefore, as a redox indicator.

Indicator Solution : 0·1g. o-dianisidine mixed with 0·5 ml. of concentrated sulphuric acid and the mixture diluted to 100 ml. with distilled water.

Procedure : To the zinc solution add 10 g. ammonium chloride and 5 ml. concentrated sulphuric acid. After beginning the titration with 0·05 M potassium ferrocyanide, add sufficient indicator to impart a red-brown colour to the solution. (If the ferrocyanide solution contains insufficient ferricyanide to give the red-brown colour, add 0·1% ferricyanide solution drop-wise till the required tint appears). At the end-point, the solution will be colourless, or, as is usual, pale-green.

Metals forming insoluble ferrocyanides interfere, and must be removed.

No experimental data nor details of the accuracy or precision of the method are given.

Diphenylcarbazone, Mercury Halide

Pale-Brown ⟶ Purple ⟶ Red-Brown

Three indicator solutions have been suggested[72] for the argentometric determination of halides in coloured solution.

Indicator Solutions :

(i) 1g. mercuric chloride and 0·5g. diphenylcarbazone in 100 ml. acetone.

(ii) 0·5g. mercuric iodide and 0·5g. diphenylcarbazone in 100 ml. acetone.

(iii) 1g. mercuric thiocyanate and 0·5g. diphenylcarbazone in 100 ml. acetone.

In a slightly acid solution the above salts do not yield sufficient ions to react with the diphenylcarbazone. The halide solution is titrated with a solution of silver nitrate till the end-point is reached, a drop of silver in excess giving sufficient Hg^{++} to produce a colour with the diphenylcarbazone.

Procedure :

Titration of Cl^- : Use indicator (i). The halide solution should be acid to the extent of 1 ml. concentrated nitric acid in a final volume of 100 ml. Add ether to the halide solution and titrate with silver nitrate till the pale-brown colour of the ether layer changes through purple to a very sharp reddish-brown end-point. (The ether prevents interference by adsorption. The red-brown mercury diphenylcarbazone complex is soluble in ether).

Titration of Br^- : Use indicator (i) with or without ether.

Titration of I^- : Use indicator (ii) without ether.

Titration of CNS^- : Use 1 ml. indicator (iii) with or without ether.

With this new type of indicator, the argentometric titration of Cl^-, Br^-, I^-, or CNS^- can be carried out in acid solution, independently of the colour of the solution.

Ceric Ammonium Sulphate, Starch

Colourless —→ Blue-Green

Bloom and McNabb[73] describe a method for the titration of silver with potassium iodide in the presence of ceric ions and starch. Oxidation of the iodide ion to iodine by the ceric ion is not permanent till the end-point is reached. During the course of the titration, a blue colour appears, but is immediately discharged on stirring.

Indicator Solutions :

(i) A 0·1 N (approx.) solution of ceric ammonium sulphate in distilled water.

(ii) A 0·5% solution of starch in distilled water.

Procedure : Transfer 10 or 20 ml. of a 0·1 N silver nitrate solution to a 200 ml. beaker. Add water and a sufficient amount of sulphuric acid to give a volume of approximately 110 ml. (concentration of acid may vary from 0·2 N–0·3 N) followed by 3 ml. starch solution and 0·1 ml. ceric ammonium sulphate solution. Titrate with 0·1 N potassium iodide. At the end-point, the solution is coloured a permanent blue-green.

Blank titrations under the above conditions but omitting the silver nitrate consume about 0·1 ml. 0·1 N potassium iodide.

The method gives good results in the presence of ferric and cupric ions.

Sodium 2,5-Cresotate

Colourless —→ Red

Sodium 2,5–cresotate reacts with uranyl acetate to form a coloured compound. Repman[74] has used this fact to indicate the end-point in the volumetric determination of phosphate by uranyl acetate.

Procedure : Place 2 ml. of sample and 2 ml. standard phosphate solution (containing 0·0025g. P_2O_5/ml.) in separate Philips' beakers. To each add 10 ml. distilled water, 2 ml. of a solution of sodium–2,5–cresotate, 1 ml. hexamine solution, and 0·5g. potassium nitrate. Heat to boiling and add dropwise from a microburette a solution of uranyl acetate. When a turbidity appears, discontinue the titration. Heat until the precipitate coagulates and continue the titration till a red colour appears. If the volumes of the solutions are not the same, add the necessary amount of water and bring both solutions to the same colour by adding uranyl acetate solution.

Benzidine Sulphate (Acetate), Cupric Ion

Sierra and Burriel[75] obtained very sharp end-points in the titration of silver solutions with potassium iodide using benzidine sulphate and cupric ions as indicator for 1 N and 0·1 N solutions, and benzidine acetate and cupric ions for 0·01 N and 0·001 N solutions.

Metals of Group III do not interfere.

The authors recommend that the acidity should not exceed about 3 ml. of N acetic acid or 2 ml. of 0·1 N nitric acid. The errors are less than 0·5%.

In a later paper, Burriel[76] describes the use of benzidine acetate and cupric nitrate as indicator in the volumetric determination of bromide with silver nitrate. The method is stated to be accurate in 0·02 N solutions.

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Design and Research Centre

INCLUDED in the new premises of the Design and Research Centre for the Gold, Silver and Jewellery Industries at Goldsmiths' Hall, which were opened by the President of the Board of Trade on November 15th, is a permanent exhibition hall, wherein a magnificent display of gold, silver and jewellery exhibits was on show during the week following the opening.

Even industries based essentially on traditional craftsmanship realise the necessity for progress, and when, on the cessation of hostilities in 1945, it was recognised that greatly increased competition would have to be faced in all world markets, the idea of a joint Design and Research Centre was discussed at a number of trade meetings at Goldsmiths' Hall. These meetings laid the foundation for the setting up of the Centre, which has greatly expanded since its inauguration four years ago.

The need for sound design in industry generally has gained increasing recognition in recent years, and the Design Section of the Centre, under its Director, Mr. S. L. Wright, has rendered valuable service to an industry in which good design has always been important.

Whilst craftsmanship has long been established in the jewellery trades, the application of scientific principles to the many problems concerned with raw materials and manufacturing methods is of more recent origin, and a study of the list of reports issued by the Research Section, under Dr. G. E. Gardem, reveals the wide range of interest for the metallurgist. Naturally electroplating and finishing processes figure prominently on the list, and investigations have been undertaken on such widely varying subjects as barrel polishing, electrolytic brightening, the electrolytic protection of silver from tarnishing, and the development of a "fireproof" sterling silver, whilst research is proceeding on "bright" silver plating, and the use of vacuum evaporation for the embellishment of costume jewellery and the like. Nor are the more basic metallurgical processes ignored, as is evident from the studies of the melting and casting of nickel silver ingots, the detection of porosity in cast sterling silver by radiography, precision casting, and the casting of low-melting-point alloys in rubber moulds.

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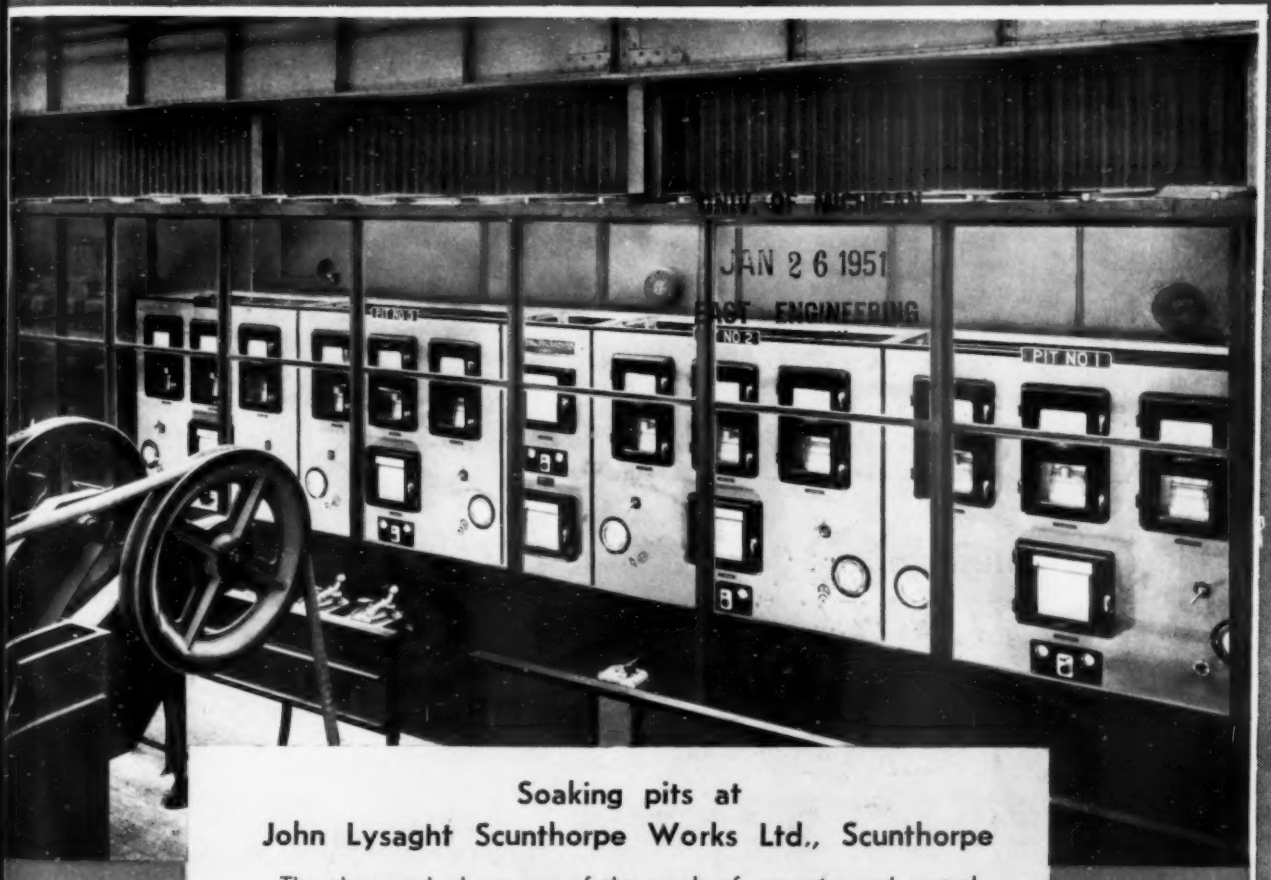

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